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Inorganic Analyses in Water Quality Control Programs: Training Manual

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Inorganic Analyses in Water Quality Control Programs

Training Manual

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A lecture/laboratory manual dealing with the analysis of selected inorganic pollutants. The manual is an instructional aid for classroom presentations to those with little or no experience in the field, but having one year (or equivalent) of college level inorganic chemistry and having basic laboratory skills including use of balances, volumetric glassware and titration assemblies. Topics in the manual are test procedures for acidity and alkalinity (titrations to pH end points), hardness (EDTA titration), chlorine (amperometric back titration), total phosphorus (persulfate digestion, ascorbic acid reduction, colorimetry), fluoride (SPADNS colorimetry and ion electrode), nitrate and nitrite (cadmium reduction, colorimetry), total and suspended solids (gravimetric), turbidity (nephelometer), and specific conductance (Wheatstone bridge conductivity meter). Other topics are sample handling; compliance methodology; accuracy, precision and error of data; elements of quality assurance programs.

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Inorganic Analyses in Water Quality Control Programs

This course is for chemists and technicians with little or no experience in inorganic analyses commonly required for the National Pollutant Discharge Elimination System (NPDES), the National Interim Primary Drinking Water Regulations (NIPDWR) and for other water quality programs. Applicants should have one year of college level inorganic chemistry and one semester of college level quantitative analysis (or equivalent). They should have basic laboratory skills including use of analytical balances, volumetric glassware and titration assemblies. They should be actively engaged in a water quality control program.

After successfully completing the course, the student will know the general classes of methods listed as approved in the Federal Register for analysis of inorganic pollutants and will be able to use the methods to measure each parameter selected for the course. He will also know how to apply quality assurance techniques to his work and how to validate his analytical accuracy and precision.

The training is a five-day course which includes classroom instruction, student performance of laboratory procedures, and discussion of each laboratory assignment and reported results.

The student will perform the test procedures for acidity and alkalinity (titrations to pH end points), hardness (EDTA titration), chlorine (amperometric back titration), total phosphorus (persulfate digestion, ascorbic acid reduction, colorimetry), fluoride (SPADNS colorimetry and ion electrode), nitrate and nitrite (cadmium reduction, colorimetry), total and suspended solids (gravimetric), turbidity (nephelometer), and specific conductance (Wheatstone bridge conductivity meter). Other topics are sample handling; compliance methodology; accuracy, precision and error of data; elements of quality assurance programs.

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SAMPLE HANDLING - FIELD THROUGH LABORATORY

I PLANNING A SAMPLING PROGRAM

A Factors to Consider:

1 Locating sampling sites

2 Sampling equipment

3 Type of sample required

a grab
b composite

4 Amount of sample required

5 Frequency of collection

6 Preservation measures, if any

B Decisive Criteria

1 Nature of the sample source

2 Stability of constituent(s) to be measured

3 Ultimate use of data

II REPRESENTATIVE SAMPLES

If a sample is to provide meaningful and valid data about the parent population, it must be representative of the conditions existing in that parent source at the sampling location.

A The container should be rinsed two or three times with the water to be collected.

B Compositing Samples

1 For some sources, a composite of samples is made which will represent the average situation for stable constituents.

2 The nature of the constituent to be determined may require a series of separate samples.

C The equipment used to collect the sample is an important factor to consider. ASTM(1) has a detailed section on various sampling devices and techniques.

D Great care must be exercised when collecting samples in sludge or mud areas and near benthic deposits. No definite procedure can be given, but careful effort should be made to obtain a representative sample.

III SAMPLE IDENTIFICATION

A Each sample must be unmistakably identified, preferably with a tag or label. The required information should be planned in advance.

B An information form preprinted on the tags or labels provides uniformity of sample records, assists the sampler, and helps ensure that vital information will not be omitted.

C Useful Identification Information includes:

1 sample identity code
2 signature of sampler
3 signature of witness
4 description of sampling location detailed enough to accommodate reproducible sampling. (It may be more convenient to record the details in the field record book).
5 sampling equipment used
6 date of collection
7 time of collection
8 type of sample (grab or composite)
9 water temperature
10 sampling conditions such as weather, water level, flow rate of source, etc.
11 any preservative additions or techniques
12 record of any determinations done in the field
13 type of analyses to be done in laboratory

IV SAMPLE CONTAINERS

A Available Materials

1 glass
2 plastic
3 hard rubber

B Considerations

1 Nature of the sample - Organics attack polyethylene.

2 Nature of constituent(s) to be determined - Cations can adsorb readily on some plastics and on certain glassware. Metal or aluminum foil cap liners can interfere with metal analyses.

3 Preservatives to be used - Mineral acids attack some plastics.

4 Mailing Requirements - Containers should be large enough to allow extra volume for effects of temperature changes during transit. All caps should be securely in place. Glass containers must be protected against breakage. Styrofoam linings are useful for protecting glassware.

C Preliminary Check

Any question of possible interferences related to the sample container should be resolved before the study begins. A preliminary check should be made using corresponding sample materials, containers, preservatives and analysis.

D Cleaning

If new containers are to be used, preliminary cleaning is usually not necessary.

If the sample containers have been used previously, they should be carefully cleaned before use.

There are several cleaning methods available. Choosing the best method involves careful consideration of the nature of the sample and of the constituent(s) to be determined.

1 Phosphate detergents should not be used to clean containers for phosphorus samples.

2 Traces of dichromate cleaning solution will interfere with metal analyses.

E Storage

Sample containers should be stored and transported in a manner to assure their readiness for use.

V SAMPLE PRESERVATION

Every effort should be made to achieve the shortest possible interval between sample collection and analyses. If there must be a delay and it is long enough to produce significant changes in the sample, preservation measures are required.

At best, however, preservation efforts can only retard changes that inevitably continue after the sample is removed from the parent population.

A Functions

Methods of preservation are relatively limited. The primary functions of those employed are:

1 to retard biological action
2 to retard precipitation or the hydrolysis of chemical compounds and complexes
3 to reduce volatility of constituents

B General Methods

1 pH control - This affects precipitation of metals, salt formation and can inhibit bacterial action.

2 Chemical Addition - The choice of chemical depends on the change to be controlled.

Mercuric chloride is commonly used as a bacterial inhibitor. Disposal of the mercury-containing samples is a problem and efforts to find a substitute for this toxicant are underway.

To dispose of solutions of inorganic mercury salts, a recommended procedure is to capture and retain the mercury salts as the sulfide at a high pH. Several firms have tentatively agreed to accept the mercury sulfide for re-processing after preliminary conditions are met.(4)

3 Refrigeration and Freezing - This is the best preservation technique available, but it is not applicable to all types of samples. It is not always a practical technique for field operations.

C Specific Methods

The EPA Methods Manual(2) includes a table summarizing the holding times and preservation techniques for several analytical procedures. This information also can be found in the standard references(1, 2, 3) as part of the presentation of the individual procedures.

D Federal Register Methods

When collecting samples to be analyzed for National Pollutant Discharge Elimination System or State Certification report purposes, one must consult the appropriate Federal Register(5) for information about sample handling procedures. When collecting samples to be analyzed for compliance with maximum contaminant levels in drinking water, consult the EPA Report(6) which includes this information.

VI METHODS OF ANALYSIS

Standard reference books of analytical procedures to determine the physical and chemical characteristics of various types of water samples are available.

A EPA Methods Manual

The Environmental Monitoring and Support Laboratory of the Environmental Protection Agency, has published a manual of analytical procedures to provide methodology for monitoring the quality of our Nation's Waters and to determine the impact of waste discharges. The title of this manual is "Methods for Chemical Analysis of Water and Wastes."(2)

For some tests, this manual refers the analyst to Standard Methods and/or to ASTM for the stepwise procedure.

B Standard Methods

The American Public Health Association, the American Water Works Association and the Water Pollution Control Federation prepare and publish a volume describing methods of water analysis. These include physical and chemical procedures. The title of this book is "Standard Methods for the Examination of Water and Wastewater."(3)

C ASTM Standards

The American Society for Testing and Materials publishes an annual "book" of specifications and methods for testing materials. The "book" currently consists of 47 parts. The part applicable to water is a book titled, "Annual Book of ASTM Standards", Part 31, Water.(1)

D Other References

Current literature and other books of analytical procedures with related information are available to the analyst.

E Federal Register Methodology

The analyst must consult the appropriate Federal Register for a listing of approved methodology if he is gathering data for National Pollutant Discharge Elimination System(5) or State Certification(5) report purposes, or to document compliance with maximum contaminant levels in drinking water(7). The Federal Register directs the user to pages in the above cited reference books where acceptable procedures can be found. The Federal Register also provides information concerning the protocol for obtaining approval to use analytical procedures other than those listed.

VII ORDER OF ANALYSES

The ideal situation is to perform all analyses shortly after sample collection. In the practical order, this is rarely possible. The allowable holding time for preserved samples is the basis for scheduling analyses.

A The allowable holding time for samples depends on the nature of the sample, the stability of the constituent(s) to be determined and the conditions of storage.

1 For some constituents and physical values, immediate determination is required, e.g. dissolved oxygen, pH.

2 Using preservation techniques, the holding times for other determinations range from 24 hours (BOD) to 7 days (COD). Metals may be held up to 6 months.(2)

3 The EPA Methods Manual(2) and Standard Methods(3) include a table summarizing holding times and preservation techniques for several analytical procedures. Additional information can be found in the standard references(1, 2, 3) as part of the presentation of the individual procedures.

4 A table with proposed holding times and preservation techniques applicable to samples collected for National Pollutant Discharge Elimination System or State Certification purposes was published in the December 18, 1979 Register(5). A similar table for drinking water samples can be found in a May, 1978 Report(6).

5 If dissolved concentrations are sought, filtration should be done in the field if at all possible. Otherwise, the sample is filtered as soon as it is received in the laboratory. A 0.45 micrometer membrane filter is recommended for reproducible filtration.

B The time interval between collection and analysis is important and should be recorded in the laboratory record book.

VIII RECORD KEEPING

The importance of maintaining a bound, legible record of pertinent information on samples cannot be over-emphasized.

A Field Operations

A bound notebook should be used. Information that should be recorded includes:

1 Sample identification records (See Part III)

2 Any information requested by the analyst as significant

3 Details of sample preservation

4 A complete record of data on any determinations done in the field. (See B, next)

5 Shipping details and records

B Laboratory Operations

Samples should be logged in as soon as received and the analyses performed as soon as possible.

A bound notebook should be used. Preprinted data forms provide uniformity of records and help ensure that required information will be recorded. Such sheets should be permanently bound.

Items in the laboratory notebook would include:

1 sample identifying code
2 date and time of collection
3 date and time of analysis
4 the analytical method used
5 any deviations from the analytical method used and why this was done
6 data obtained during analysis
7 results of quality control checks on the analysis
8 any information useful to those who interpret and use the data
9 signature of the analyst

IX SUMMARY

Valid data can be obtained only from a representative sample, unmistakably identified, carefully collected and stored. A skilled analyst, using approved methods of analyses and performing the determinations within the prescribed time limits, can produce data for the sample. This data will be of value only if a written record exists to verify sample history from the field through the laboratory.

REFERENCES

1 ASTM Annual Book of Standards, Part 31, Water, 1975.

2 Methods for Chemical Analysis of Water and Wastes, EPA-EMSL Cincinnati, Ohio 45268, 1979.

3 Standard Methods for the Examination of Water and Wastewater, 14th edition APHA-AWWA-WPCF, 1975.

4 Dean, R., Williams, R. and Wise, R., Disposal of Mercury Wastes from Water Laboratories, Environmental Science and Technology, October, 1971.

5 Federal Register, "Guidelines Establishing Test Procedures for the Analysis of Pollutants," Vol. 41, No. 232, December 1, 1976, pp pp 52780-52786. Also, Vol. 44, No. 244, December 18, 1979 pp 75028-75052 presents proposed changes. The latter is scheduled for finalization after January, 1981.

6 "Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies - Criteria and Procedures," U.S. EPA Report No. 600/8-78-008, May, 1978.

7 Federal Register, "National Interim Primary Drinking Water Regulations," Vol. 40, No. 248, December 24, 1975, pp 59566-59574. Also, "Interim Primary Drinking Water Regulations; Amendments," Vol. 45, No. 168, August 27, 1980, pp 57332-57346.

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METHODOLOGY FOR CHEMICAL ANALYSIS OF WATER AND WASTEWATER

I INTRODUCTION

This outline deals with chemical methods which are commonly performed in water quality laboratories. Although a large number of constituents or properties may be of interest to the analyst, many of the methods employed to measure them are based on the same analytical principles. The purpose of this outline is to acquaint you with the principles involved in commonly-used chemical methods to determine water quality.

II PRE-TREATMENTS

For some parameters, a preliminary treatment is required before the analysis begins. These treatments serve various purposes.

A Distillation - To isolate the constituent by heating a portion of the sample mixture to separate the more volatile part(s), and then cooling and condensing the resulting vapor(s) to recover the volatilized portion.

B Extraction - To isolate/concentrate the constituent by shaking a portion of the sample mixture with an immiscible solvent in which the constituent is much more soluble.

C Filtration - To separate undissolved matter from a sample mixture by passing a portion of it through a filter of specified size. Particles that are dissolved in the original mixture are so small that they stay in the sample solution and pass through the filter.

D Digestion - To change constituents to a form amenable to the specified test by heating a portion of the sample mixture with chemicals.

III METERS

For some parameters, meters have been designed to measure that specific constituent or property.

A pH Meters

pH (hydrogen ion concentration) is measured as a difference in potential across a glass membrane which is in contact with the sample and with a reference solution. The sensor apparatus might be combined into one probe or else it is divided into an indicating electrode (for the sample) and a reference electrode (for the reference solution). Before using, the meter must be calibrated with a solution of known pH (a buffer) and then checked for proper operation with a buffer of a different pH value.

B Dissolved Oxygen Meters

Dissolved oxygen meters measure the production of a current which is proportional to the amount of oxygen gas reduced at a cathode in the apparatus. The oxygen gas enters the electrode through a membrane, and an electrolyte solution or gel acts as a transfer and reaction media. Prior to use the meter must be calibrated against a known oxygen gas concentration.

C Conductivity Meters

Specific conductance is measured with a meter containing a Wheatstone bridge which measures the resistance of the sample solution to the transmission of an electric current. The meter and cell are calibrated according to the conductance of a standard solution of potassium chloride measured at 25°C by a "standard" cell with electrodes one cm square spaced one cm apart. This is why results are called "specific" conductance.

D Turbidimeters

A turbidimeter compares the intensity of light scattered by particles in the sample under defined conditions with the intensity of light scattered by a standard reference suspension.

IV SPECIFIC ION ELECTRODES

Just as the conventional glass electrode for pH develops an electrical potential in response to the activity of hydrogen ion in solution, the specific ion electrode develops an electrical potential in response to the activity of the ion for which the electrode is specific. The potential and activity are related according to the Nernst equation. Simple analytical techniques can be applied to convert activity to an expression of concentration.

These electrodes are used with a pH meter with an expanded mV scale or with a specific ion meter. Two examples are the ammonia and fluoride electrodes.

A Ammonia

The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

B Fluoride

The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^-(0.3), F^-(0.001) LaF/test solution/SCE/. It is used in conjunction with a standard single junction reference electrode.

V GENERAL ANALYTICAL METHODS

A Volumetric Analysis

Titrations involve using a buret to measure the volume of a standard solution of a substance required to completely react with the constituent of interest in a measured volume of sample. One can then calculate the original concentration of the constituent of interest.

There are various ways to detect the end point when the reaction is complete.

1 Color change indicators

The method may utilize an indicator which changes color when the reaction is complete. For example, in the Chemical Oxygen Demand Test the indicator, ferroin, gives a blue-green color to the mixture until the oxidation-reduction reaction is complete. Then the mixture is reddish-brown.

Several of these color-change titrations make use of the iodometric process whereby the constituent of interest quantitatively releases free iodine. Starch is added to give a blue color until enough reducing agent (sodium thiosulfate or phenylarsine oxide) is added to react with all the iodine. At this end point, the mixture becomes colorless.

2 Electrical property indicators

Another way to detect end points is a change in an electrical property of the solution when the reaction is complete. In the chlorine titration a cell containing potassium chloride will produce a small direct current as long as free chlorine is present. As a reducing agent (phenylarsine oxide) is added to reduce the chlorine, the microammeter which measures the existing direct current registers a lower reading on a scale. By observing the scale, the end point of total reduction of chlorine can be determined because the direct current ceases.

3 Specified end points

For acidity and alkalinity titrations, the end points are specified pH values for the final mixture. The pH values are those existing when common acidity or alkalinity components have been neutralized. Thus acidity is determined by titrating the sample with a standard alkali to pH 8.2 when carbonic acid would be neutralized to $(HCO_3)^-$. Alkalinity (except for highly acidic samples) is determined by titrating the sample with a standard acid to pH 4.5 when the carbonate present has been converted to carbonic acid. pH meters are used to detect the specified end points.

B Gravimetric Procedures

Gravimetric methods involve direct weighing of the constituent in a container. An empty container is weighed, the constituent is separated from the sample mixture and isolated in the container, then the container with the constituent is weighed. The difference in the weights of the container before and after containing the constituent represents the weight of the constituent.

The type of container depends on the method used to separate the constituent from the sample mixture. In the solids determinations, the container is an evaporating dish (total or dissolved) or a glass fiber filter disc in a crucible (suspended). For oil and grease, the container is a flask containing a residue after evaporation of a solvent.

C Combustion

Combustion means to add oxygen. In the Total Organic Carbon Analysis, combustion is used within an instrument to convert carbonaceous material to carbon dioxide. An infrared analyzer measures the carbon dioxide.

VI PHOTOMETRIC METHODS

These methods involve the measurement of light that is absorbed or transmitted quantitatively either by the constituent of interest or else by a substance containing the constituent of interest which has resulted from some treatment of the sample. The quantitative aspect of these photometric methods is based on applying the Lambert-Beer Law which established that the amount of light absorbed is quantitatively related to the concentration of the absorbing medium at a given wavelength and a given thickness of the medium through which the light passes.

Each method requires preparing a set of standard solutions containing known amounts of the constituent of interest. Photometric values are obtained for the standards. These are used to draw a calibration (standard) curve by plotting photometric values against the concentrations. Then, by locating the photometric value for the sample on this standard curve, the unknown concentration in the sample can be determined.

A Atomic Absorption

Atomic Absorption (AA) instruments utilize absorption of light of a characteristic wavelength. This form of analysis involves aspirating solutions of metal ions (cations) or molecules containing metals into a flame where they are reduced to individual atoms in a ground electrical state. In this condition, the atoms can absorb radiation of a wavelength characteristic for each element. A lamp containing the element of interest as the cathode is used as a source to emit the characteristic line spectrum for the element to be determined.

The amount of energy absorbed is directly related to the concentration of the element of interest. Thus the Lambert-Beer Law applies. Standards can be prepared and tested and the resulting absorbance values can be used to construct a calibration (standard) curve. Then the absorbance value for the sample is located on this curve to determine the corresponding concentration.

Once the instrument is adjusted to give optimum readings for the element of interest, the testing of each solution can be done in a matter of seconds. Many laboratories wire recorders into their instruments to rapidly transcribe the data, thus conserving time spent on this aspect of the analysis. Atomic absorption techniques are generally used for metals and semi-metals in solution or else solubilized through some form of sample processing. For mercury, the principle is utilized but the absorption of light occurs in a flameless situation with the mercury in the vapor state and contained in a closed glass cell.

B Flame Emission

Flame emission photometry involves measuring the amount of light given off by atoms drawn into a flame. At certain temperatures, the flame raises the electrons in atoms to a higher energy level. When the electrons fall back to a lower energy level, the atoms lose (emit) radiant energy which can be detected and measured.

Again standards must be prepared and tested to prepare a calibration (standard) curve. Then the transmission value of the sample can be located on the curve to determine its concentration.
Many atomic absorption instruments can be used for flame emission photometry. Sodium and potassium are very effectively determined by the emission technique.

However, for many elements, absorption analysis is more sensitive because there are a great number of unexcited atoms in the flame which are available to absorb the radiant energy.

C Colorimetry

Colorimetric analyses involve treating standards which contain known concentrations of the constituent of interest and also the sample with reagents to produce a colored solution. The greater the concentration of the constituent, the more intense will be the resulting color.

The Lambert-Beer Law which relates the absorption of light to the thickness and concentration of the absorbing medium applies. Accordingly, a spectrophotometer is used to measure the amount of light of appropriate wavelength which is absorbed by the same thickness of each solution. The results from the standards are used to construct a calibration (standard) curve. Then the absorbance value for the sample is located on this curve to determine the corresponding concentration.

Many of the metals and several other parameters (phosphorus, ammonia, nitrate, nitrite, etc.) are determined in this manner.

VII GAS-LIQUID CHROMATOGRAPHY

Chromatography techniques involve a separation of the components in a mixture by using a difference in the physical properties of the components. Gas-Liquid Chromatography (GLC) involves separation based on a difference in the properties of volatility and solubility. The method is used to determine algicides, chlorinated organic compounds and pesticides.

The sample is introduced into an injector block which is at a high temperature (e.g. 210°C), causing the liquid sample to volatilize. An inert carrier gas transports the sample components through a liquid held in place as a thin film on an inert solid support material in a column.

Sample components pass through the column at a speed partly governed by the relative solubility of each in the stationary liquid. Thus the least soluble components are the first to reach the detector. The type of detector used depends on the class of compounds involved. All detectors function to sense and measure the quantity of each sample component as it comes off the column. The detector signals a recorder system which registers a response.

As with other instrumental methods, standards with known concentrations of the substance of interest are measured on the instrument. A calibration (standard) curve can be developed and the concentration in a sample can be determined from this graph.

Gas-liquid chromatography methods are very sensitive (nanogram, picogram quantities) so only small amounts of samples are required. On the other hand, this extreme sensitivity often necessitates extensive clean-up of samples prior to GLC analysis.

VIII AUTOMATED METHODS

The increasing number of samples and measurements to be made in water quality laboratories has stimulated efforts to automate these analyses. Using smaller amounts of sample (semi-micro techniques), combining reagents for fewer measurements per analysis, and using automatic dispensers are all means of saving analytical time.

However, the term "automated laboratory procedures" usually means automatic introduction of the sample into the instrument, automatic treatment of the sample to test for a component of interest, automatic recording of data and, increasingly, automatic calculating and print-out of data. Maximum automation systems involve continuous sampling direct from the source (e.g. an in-place probe) with telemetering of results to a central computer.

Automated methods, especially those based on colorimetric methodology, are recognized for several water quality parameters including alkalinity, ammonia, nitrate, nitrite, phosphorus, and hardness.

IX SOURCES OF PROCEDURES

Details of the procedure for an individual measurement can be found in reference books. There are three particularly-recognized books of procedures for water quality measurements.

A Standard Methods(1)

The American Public Health Association, the American Water Works Association and the Water Pollution Control Federation prepare and publish "Standard Methods for the Examination of Water and Wastewater." As indicated by the list of publishers, this book contains methods developed for use by those interested in water or wastewater treatment.

B ASTM Standards(2)

The American Society for Testing and Materials publishes an "Annual Book of ASTM Standards" containing specifications and methods for testing materials. The "book" currently consists of 47 parts. The part applicable to water was formerly Part 23. It is now Part 31, Water.

The methods are chosen by approval of the membership of ASTM and are intended to aid industry, government agencies and the general public. Methods are applicable to industrial waste waters as well as to other types of water samples.

C EPA Methods Manual(3)

The United States Environmental Protection Agency publishes a manual of "Methods for Chemical Analysis of Water and Wastes."

EPA developed this manual to provide methodology for monitoring the quality of our Nation's waters and to determine the impact of waste discharges. The test procedures were carefully selected to meet these needs, using Standard Methods and ASTM as basic references. In many cases, the EPA manual contains completely described procedures because they modified methods from the basic references. Otherwise, the manual cites page numbers in the two references where the analytical procedures can be found.

X ACCURACY AND PRECISION

A Of the Method

One of the criteria for choosing methods to be used for water quality analysis is that the method should measure the desired property or constituent with precision, accuracy, and specificity sufficient to meet data needs. Standard references, then, include a statement of the precision and accuracy for the method which is obtained when (usually) several analysts in different laboratories used the particular method.

B Of the Analyst

Each analyst should check his own precision and accuracy as a test of his skill in performing a test. According to the U. S. EPA Handbook for Analytical Quality Control(4), he can do this in the following manner.

To check precision, the analyst should analyze samples with four different concentrations of the constituent of interest, seven times each. The study should cover at least two hours of normal laboratory operations to allow changes in conditions to affect the results. Then he should calculate the standard deviation of each of the sets of seven results and compare his values for the lowest and highest concentrations tested with the standard deviation value published for that method in the reference book. (It may be stated as % relative standard deviation. If so, calculate results in this form.) An individual should have better values than those averaged from the work of several analysts.

To check accuracy, he can use two of the samples used to check precision by adding a known amount (spike) of the particular constituent in quantities to double the lowest concentration used, and to bring an intermediate concentration to approximately 75% of the upper limit of application of the method. He then analyzes each of the spiked samples seven times, then calculates the average of each set of seven results. To calculate accuracy in terms of % recovery, he will also need to calculate the average of the results he got when he analyzed the unspiked samples (background). Then:

$$\% \text{ Recovery} = \left[\frac{\text{observed} - \text{background}}{\text{spike}}\right] \times 100$$

The actual calculation involves volume-concentration calculations for each term.

If the published accuracy is stated as % bias, subtract 100% from % recovery to compare results. Again, the individual result should be better than the published figure derived from the results of several analysts.

C Of Daily Performance

Even after an analyst has demonstrated his personal skill in performing the analysis, a daily check on precision and accuracy should be done. About one in every ten samples should be a duplicate to check precision and about one in every ten samples should be spiked to check accuracy.

It is also beneficial to participate in inter-laboratory quality control programs. The U.S. EPA provides reference samples at no charge to laboratories. These samples serve as independent checks on reagents, instruments or techniques; for training analysts or for comparative analyses within the laboratory. There is no certification or other formal evaluative function resulting from their use.

XI SELECTION OF ANALYTICAL PROCEDURES

Standard sources$^{(1, 2, 3)}$ will, for most parameters, contain more than one analytical procedure. Selection of the procedure to be used in a specific instance involves consideration of the use to be made of the data. In some cases, one must use specified procedures. In others, one may be able to choose among several methods.

A NPDES Permits and State Certifications

A specified analytical procedure must be used when a waste constituent is measured:

1 For an application for a National Pollutant Discharge Elimination System (NPDES) permit under Section 402 of the Federal Water Pollution Control Act (FWPCA), as amended.

2 For reports required to be submitted by dischargers under NPDES.

3 For certifications issued by States pursuant to Section 401 of the FWPCA, as amended.

Analytical procedures to be used in these situations must conform to those specified in Title 40, Chapter 1, Part 136, of the Code of Federal Regulations (CFR). The listings in the CFR usually cite two different procedures for a particular measurement.

The CFR also provides a system of applying to EPA for permission to use methods not cited in the CFR. Approval of alternative methods for nationwide use will be published in the Federal Register.

B Ambient Water Quality Monitoring

For Ambient Water Quality Monitoring, analytical procedures have not been specified by regulations. However, the selection of procedures to be used should receive attention. Use of those listed in the CFR is strongly recommended. If any of the data obtained is going to be used in connection with NPDES permits, or may be used as evidence in a legal proceeding, use of procedures listed in the CFR is again strongly recommended.

C Drinking Water Monitoring

In December, 1975, National Interim Primary Drinking Water Regulations to be effective June 24, 1977 were published in the Federal Register in Title 40, Chapter 1, Subchapter D, Part 141. The publication includes specification of analytical procedures to be used when determining compliance with the maximum contaminant levels of required parameters.

Because of the low concentrations involved in the regulations, there is often just one analytical method cited for each parameter.

Individuals or organizations may apply to EPA for permission to use methods not cited in the above. Approval of alternative methods for nationwide use will be published in the Federal Register.

XII FIELD KITS

Field kits have been devised to perform analyses outside of the laboratory. The kit may contain equipment and reagents for only one test or for a variety of measurements. It may be purchased or put together by an agency to serve its particular needs.

Since such kits are devised for performing tests with minimum time and maximum simplicity, the types of labware and reagents employed usually differ significantly from the equipment and supplies used to perform the same measurement in a laboratory.

A Shortcomings

Field conditions do not accommodate the equipment and services required for pretreatments like distillation and digestion. Nor is it practical to carry and use calibrated glassware like burets and volumetric pipets. Other problems are preparation, transport and storage of high quality reagents, of extra supplies required to test for and remove sample interferences before making the measurement, and of instruments which are very sensitive in detecting particular constituents. One just cannot carry and set up laboratory facilities in the field which are equivalent to stationary analytical facilities.

B Uses

Even though the results of field tests are usually not as accurate and precise as those performed in the laboratory, such tests do have a place in water quality programs.

In situations where only an estimate of the concentrations of various constituents is required, field tests serve well. They are invaluable sources of information for planning a full-scale sampling/testing program when decisions must be made regarding location of sampling sites, schedule of sample collection, dilution of samples required for analysis, and treatment of samples required to remove interferences to analyses.

C NPDES Permits and State Certification

Kit methods are not approved for obtaining data required for NPDES permits or State construction certifications. If one judges that such a method is justifiable for these purposes, he must apply to EPA for permission to use it.

D Drinking Water Monitoring

The DPD test kit for residual chlorine is approved in the December, 1975 Federal Register for monitoring drinking water in cases where chlorine tests are substitutes for microbiological tests.

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Descriptors: Analysis, Chemical Analysis, Methodology, Wastewater, Water Analysis

STATISTICS FOR CHEMISTS

I INTRODUCTION

A Statistics may be defined, for our purpose, as a collection of methods which have been developed for handling numerical data pertaining to samples or portions of entire populations.

B The statistical methods with which we will concern ourselves deal with the presentation and analysis of numerical data from samples.

II FREQUENCY

A Definitions

1 Frequency - indicates how many times a particular score occurs in a collection of data

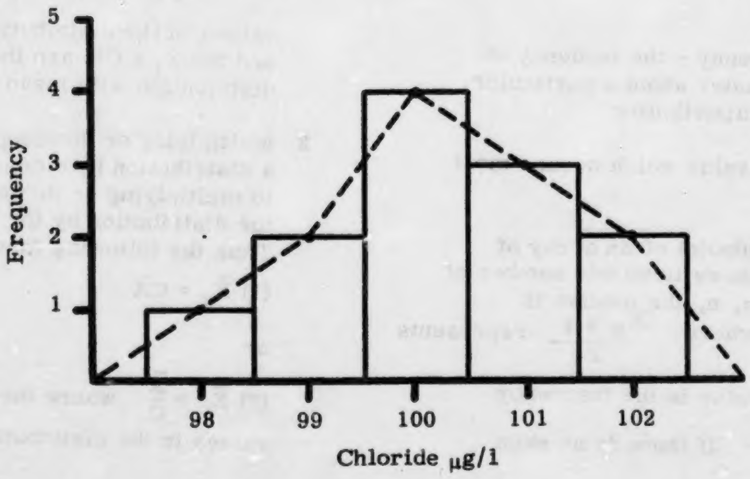
2 Frequency table - a tabular arrangement of data, ranked in ascending or descending order of magnitude, together with the corresponding frequencies

3 Frequency histogram - a set of rectangles having bases on a horizontal axis with centers at the given scores and heights equal to the corresponding frequencies (See Figure 1)

4 Frequency polygon - a line graph of frequencies plotted against scores (can be obtained by connecting midpoints of tops of rectangles in the frequency histogram) (See Figure 1)

Figure 1

Frequency Histogram & Frequency Polygon



B Application

Consider the application of the above definitions to the following set of data, obtained from twelve determinations for chloride in water.

Results (µg/l)

100	101	99
101	100	100
99	102	100
98	101	102

Table 1

Frequency Table

Chloride (µg/l)	Frequency
98	1
99	2
100	4
101	3
102	2

III MEASURES OF CENTRAL TENDENCY

A Definitions

1 Central tendency - the tendency of values to cluster about a particular value in the distribution

2 Mode - that value which occurs most frequently

3 Median - midpoint of an array of scores. If there is an odd number of observations, n, the median is $X_{\frac{n+1}{2}}$ where $X_{\frac{n+1}{2}}$ represents the $\frac{n+1}{2}$ value in the frequency distribution. If there is an even number of observations the median is $\dfrac{X_{\frac{n}{2}} + X_{\frac{n}{2}+1}}{2}$, the average of the middle two scores.

4. Mean - arithmetic average of all the values in the sample distribution, denoted by $\overline{X}$. The formula for calculating the sample mean is

$$\overline{X} = \frac{X_1 + X_2 + X_3 \dots X_n}{n}$$

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

$\overline{X} = \frac{\Sigma X_i}{n}$ where there are n number of values.

B Aids in calculation of the mean

Application of the following two statements can reduce errors and amount of time spent in calculating the mean of a distribution.

1 Adding or subtracting a constant to or from each score in a distribution is equivalent to adding or subtracting the same constant to or from the mean of the distribution. Thus the following formula:

$\overline{X}_c = \overline{X} \pm C$ where the X_i's are the values in the distribution with mean $\overline{X}$, and the $X_i \pm C$'s are the values in the distribution with mean $\overline{X}_c$.

2 Multiplying or dividing each score in a distribution by a constant is equivalent to multiplying or dividing the mean of the distribution by the same constant. Thus the following formulas:

(1) $\overline{X}_c = C\overline{X}$

or

(2) $\overline{X}_c = \frac{\overline{X}}{C}$ where the X_i's are the values in the distribution with mean $\overline{X}$,

and the CX_i's or the $\frac{X_i}{C}$'s are the values in the distribution with mean $\bar{X}_c$

C Application

Consider the application of the above definitions to the previously mentioned set of data, obtained from twelve determinations for chloride in water, shown in Table 1.

1 Mode = 100

2 $$\text{Median} = \frac{X_{\frac{n}{2}} + X_{\frac{n}{2}+1}}{2} = \frac{X_6 + X_7}{2}$$

$$= \frac{100 + 100}{2} = 100$$

3 $$\text{Mean} = \frac{\Sigma X_i}{n}$$

$$= \frac{98 + 2\,(99) + 4\,(100) + 3\,(101) + 2\,(102)}{12}$$

$$= 100.25$$

4 Aid in Calculation

Consulting Table 1 and observing that the values are in the neighborhood of 100 we might subtract 100 from each score and obtain the following distribution:

Table 2

Frequency Table

Chloride (µg/l)	Frequency
-2	1
-1	2
0	4
1	3
2	2

Denote the mean of the distribution in Table 1 by $\bar{X}_c$. If we add 100 to each score in the distribution in Table 2, we obtain the scores in the distribution in Table 1; likewise if we add 100 to the mean, X, of the distribution in Table 2, we obtain the mean, $\bar{X}_c$, of the distribution in Table 1.

Thus $$\bar{X}_c = \bar{X} + 100$$

$$\bar{X}_c = \frac{\Sigma X}{n} + 100$$

$$\bar{X}_c = \frac{1(-2) + 2(-1) + 4(0) + 3(1) + 2(2)}{12} + 100$$

$$\bar{X}_c = .25 + 100 = 100.25$$

IV MEASURES OF DISPERSION

A Definitions

1 Dispersion - spread or variability of observations in a distribution

2 Range - the difference between the highest value and the lowest value

$$R = \max - \min$$

3 Average deviation - the sum of the deviations of the values from their mean, without regard to sign, divided by the total number of data values (n)

The formula for calculating the average deviation is:

$$d = \frac{\Sigma |X_i - \bar{X}|}{n}$$

4 Average deviation of the mean (D) - the average deviation of individual data items from the mean (d) divided by the square root of the number of data items (n)

The definition of the average deviation of the mean can be expressed by the formula:

$$D = \frac{d}{\sqrt{n}}$$

5 Variance - the sum of the squares of the deviations of the values from their mean divided by the total number of data values (n) minus 1

The definition of the variance can be expressed by the following formula:

$$s^2 = \frac{\Sigma(X_i - \overline{X})^2}{n - 1}$$

6 Standard deviation - the square root of the variance

The definition of the standard deviation can be expressed by the following formula:

$$s = \sqrt{\frac{\Sigma(X_i - \overline{X})^2}{n - 1}}$$

However, the formula commonly used because of its adaptability to the hand calculator is the following:

$$s = \sqrt{\frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n - 1}}$$ where there are n number of values.

7 Standard deviation of the mean (S) - the standard deviation of individual data items (s) divided by the square root of the number of data items (n)

The definition of the standard deviation of the mean can be expressed by the formula:

$$S = \frac{s}{\sqrt{n}}$$

8 Relative standard deviation - the standard deviation (s) expressed as a fraction of the mean, $\frac{s}{\overline{X}}$

The relative standard deviation is often expressed as a percent. It is then referred to as the coefficient of variation (V), or % relative standard deviation:

$$V = \frac{s}{\overline{X}} \times 100$$

The relative standard deviation is particularly helpful when comparing the precision of a number of determinations on a given substance at different levels of concentration.

B Aids in Calculation

Application of the following statements can reduce errors and amount of time spent in calculating the variance or standard deviation of a distribution.

1 Adding or subtracting a constant to or from each score in a distribution doesn't affect the variance or standard deviation of the distribution.

Thus the following formulas:

(1) $s_c^2 = s^2$

(2) $s_c = s$

where the X_i's are the values in the distribution with variance s^2 and standard deviation s, and the $X_i \pm C$'s are the values in the distribution with variance s_c^2 and standard deviation s_c.

2 Multiplying or dividing each score in a distribution by a constant is equivalent to multiplying or dividing the variance of that distribution by the square of the same constant.

Thus the following formulas:

(1) $s_c{}^2 = C^2 s^2$

(2) $s_c{}^2 = \frac{s^2}{C^2}$

where the X_i's are the values in the distribution with variance s^2, and the CX_i's or the $\frac{X_i}{C}$'s are the values in the distribution with variance $s_c{}^2$.

3 Multiplying or dividing each score in a distribution by a constant is equivalent to multiplying or dividing the standard deviation of that distribution by the same constant.

Thus the following formulas:

(1) $s_c = Cs$

or

(2) $s_c = \frac{s}{C}$

where the X_i's are the values in the distribution with standard deviation s, and the CX_i's or the $\frac{X_i}{C}$'s are the values in the distribution with standard deviation s_c.

C Application

Consider the application of the above definitions to the previously mentioned set of data, obtained from twelve determinations for chloride in water, shown in II B, Table 1.

1 Range = 102 - 98 = 4

2 Average deviation - $d = \frac{\Sigma|X_i - \bar{X}|}{n}$

n	X_i	$\|X_i - \bar{X}\|$	$n\|X_i - \bar{X}\|$
1	98	2.25	2.25
2	99	1.25	2.50
4	100	.25	1.00
3	101	.75	2.25
2	102	1.75	3.50
	$\bar{X}$ = 100.25		11.50

$$d = \frac{\Sigma|X_i - \bar{X}|}{n} = \frac{11.50}{12} = .96$$

3 Average deviation of the mean -

$$D = \frac{d}{\sqrt{n}}$$

Using calculations from number 2,

$$D = \frac{d}{\sqrt{n}} = \frac{0.96}{\sqrt{12}} = \frac{0.96}{3.46} = 0.28$$

4 Variance - $s^2 = \frac{\Sigma(X_i - \bar{X})^2}{n-1}$

n	X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$	$n(X_i - \bar{X})^2$
1	98	-2.25	5.06	5.06
2	99	-1.25	1.56	3.12
4	100	- .25	.06	.24
3	101	+ .75	.56	1.68
2	102	+1.75	3.06	6.12
				16.22

$$s^2 = \frac{\Sigma(X_i - \bar{X})^2}{n - 1} = \frac{16.22}{11} = 1.47$$

5 **Standard deviation** - $s = \sqrt{\dfrac{\Sigma X_i^2 - \dfrac{(\Sigma X_i)^2}{n}}{n - 1}}$

n	X_i	nX_i	X^2_i	nX^2_i
1	98	98	9604	9604
2	99	198	9801	19602
4	100	400	10000	40000
3	101	303	10201	30603
2	102	204	10404	20808
		1203		120617

$$s = \sqrt{\frac{120617 - \frac{1203^2}{12}}{11}} = \sqrt{\frac{120617 - 120601}{11}}$$

$$s = \sqrt{\frac{16}{11}} = 1.21$$

6 **Aid in calculation**

Recalling that adding or subtracting a constant to each score in the distribution doesn't affect the variance or the standard deviation of the distribution we can simplify the computations by first subtracting 100 from each score in the distribution, thus obtaining the frequency distribution shown in Table 2.

n	X_i-C	n(X_i-C)	$(X_i\text{-}C)^2$	$n(X_i\text{-}C)^2$
1	-2	-2	4	4
2	-1	-2	1	2
4	0	0	0	0
3	1	3	1	3
2	2	4	4	8
		3		17

$$s^2 = \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n - 1}$$

$$s^2 = \frac{17 - \frac{(3)^2}{12}}{11} = \frac{16.25}{11} = 1.48$$

$$s = \sqrt{\frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n - 1}} = \sqrt{1.48} = 1.22$$

7 **Standard deviation of the mean** -

$$S = \frac{s}{\sqrt{n}}$$

Using calculations from number 6,

$$S = \frac{s}{\sqrt{n}} = \frac{1.22}{\sqrt{12}} = \frac{1.22}{3.46} = 0.35$$

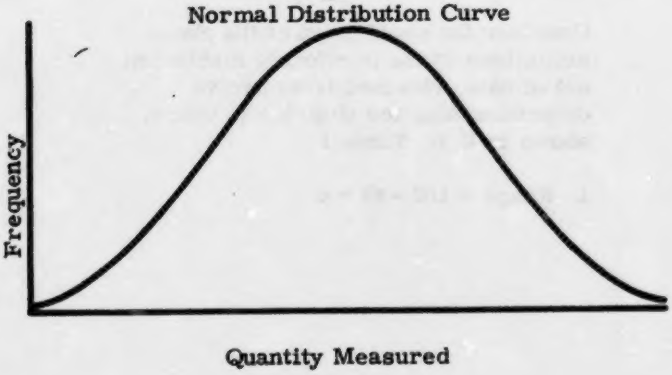
8 **Relative standard deviation expressed as a percent (coefficient of variation)**

$$V = \frac{s}{\overline{X}} \times 100$$

Using calculations from number 6 for $s = 1.22$ and from number 2 for $\overline{X} = 100.25$,

$$V = \frac{s}{\overline{X}} = \frac{1.22}{100.25} \times 100 = 1.21\%$$

Figure 2
Normal Distribution Curve



V INTRODUCTION TO NORMAL DISTRIBUTION CURVE

A Statistics deals with theoretical curves which are smoother than frequency polygons, obtained from experiments in real life. However, frequency distributions or frequency polygons of experimental data often approximate a mathematical function called the "normal" distribution curve. (See Figure 2)

As shown in Figure 3, the frequency polygon for the 12 determinations for chloride in water is a fairly good approximation of the normal curve. If, however, in the chloride determinations we had obtained 103 instead of 98 and 104 instead of 99 this distribution would not have been a good approximation of the normal curve, as is shown in Figure 4.

Figure 3

Comparison of Normal Curve and Frequency Polygon

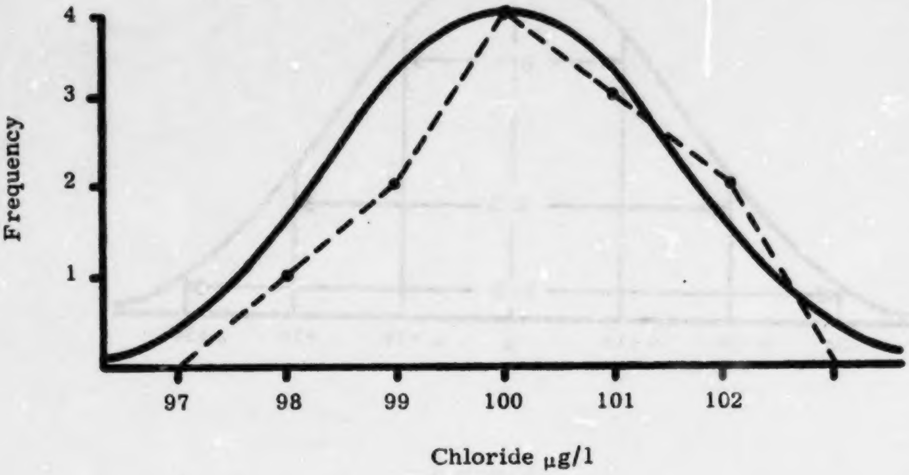
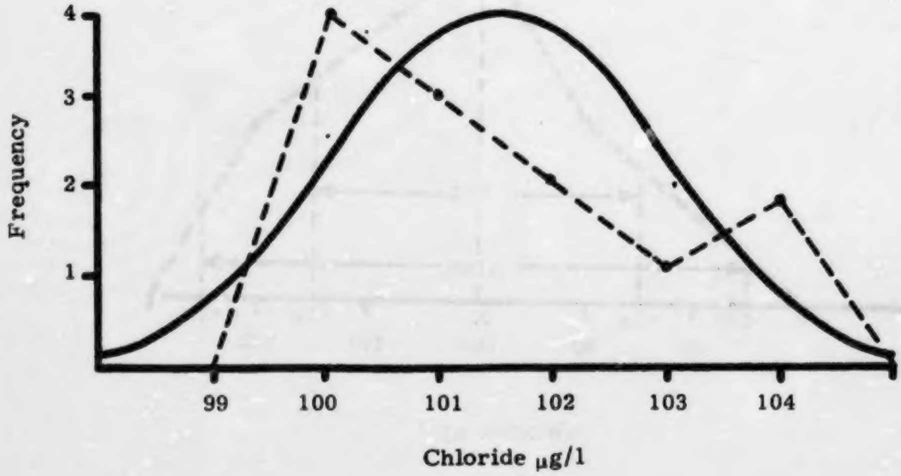


Figure 4

Comparison of Normal Curve and Frequency Polygon



B **If a frequency distribution is a good approximation of the normal curve, we can use some facts about the normal curve to give us information about the frequency distribution.**

Figure 5 shows the normal distribution in terms of the population mean μ, and the standard deviation of the population σ, and gives the percent of area under the curve between certain points.

Figure 5

Normal Distribution Curve

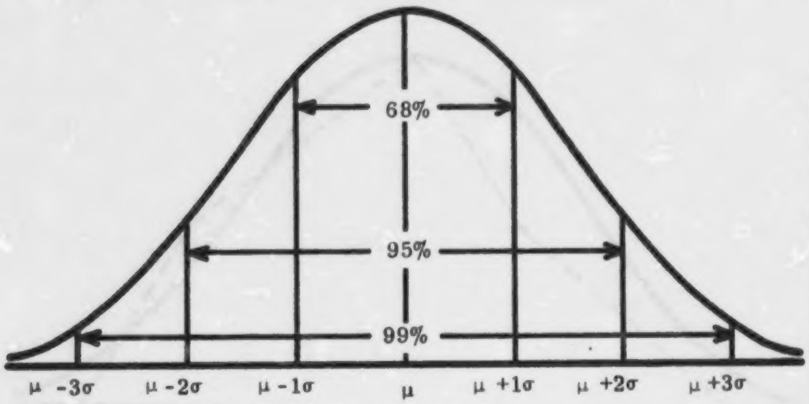
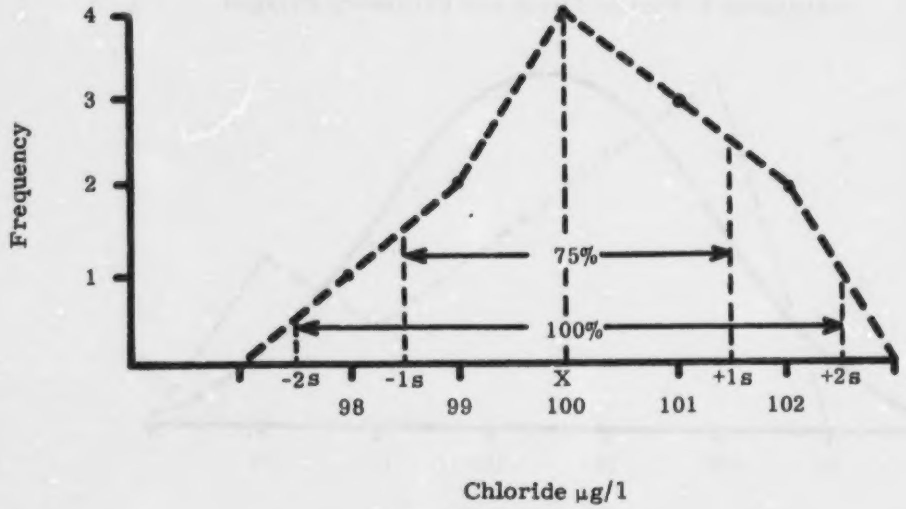


Figure 6

Frequency Distribution Polygon



We may check the distribution of sample data to see if it is a "normal" distribution in the following manner. Substitute the value of the sample mean ($\overline{X}$) for the value of the midline and substitute the value of the sample standard deviation (s) for the limits of the value spans where we might expect certain percentages of the data items to occur. Then we can check the number of data items which actually do occur within these value spans.

Figure 6 demonstrates this application using the chloride data values from Table 1. The data values are marked on the horizontal line and the frequency of the occurrence of each value is marked on the vertical. The midline of the distribution is marked at the value of the sample mean ($\overline{X}$ = 100, See III C 3). The value of the sample standard deviation (s = 1.21, See IV C 5) is used to mark value areas under the curve where different percentages of data values will probably occur. Thus, for the area $\overline{X} \pm 1s$, $\overline{X} - 1s = 98.79$ and $\overline{X} + 1\ s = 101.21$. Therefore, according to the normal distribution curve shown in Figure 5, we might expect about 68% of the data items to have values between 99 and 101. (The values are rounded to whole numbers since the data values are thus recorded).

Consulting Table 1, we find that 75% or 9 of the 12 data items have values in this range. This percentage is shown in Figure 6 by the frequency polygon for the data shown earlier in Figure 3.

Likewise assuming a normal distribution, we would expect 95% of the observations to lie within $\pm 2\sigma$'s from the population mean. In fact, 100% of the observations were within $\pm$ 2 s's from the sample mean.

In both cases the observed percentages are reasonably close to the expected percentages. Other tests exist for determining whether or not a frequency distribution might reasonably be assumed to approximate the normal distribution.

It would be good to become as familiar as possible with the normal distribution since an underlying normal distribution is assumed for many statistical tests of hypothesis.

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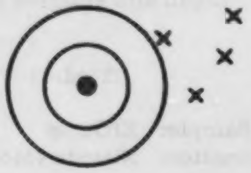
Descriptors: Graphic Methods, Quality Control, Statistical Methods, Statistics

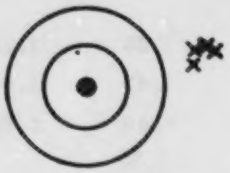
ACCURACY-PRECISION-ERROR

I INTRODUCTION

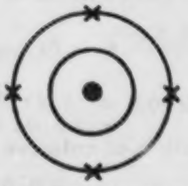
An analytical method is subject to errors. These errors may affect the accuracy of the method because they introduce bias into the results. There are other types of errors which affect the precision of the method because they produce random fluctuations in the data. The most desirable situation for the analyst is shown in the diagram in Figure 1 where the results are both precise and accurate.



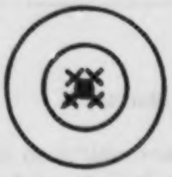
IMPRECISE AND INACCURATE



PRECISE BUT INACCURATE



ACCURATE BUT IMPRECISE



PRECISE AND ACCURA

Figure 1. PRECISION AND ACCURACY

A Accuracy

For results to be accurate, the analysis used must give values close to the true value.(See Figure 1)

B Precision

Precision is the degree of agreement among results obtained by repeated measurements on a single sample under a given set of conditions. It is a measure of the degree to which results "check." (See Figure 1)

C Note

It is possible to have precision without accuracy. (See Figure 1)

II DETERMINATE ERROR AND ACCURACY

A determinate error is one which contributes a constant error or bias to results, causing them to be inaccurate. This constant error makes it possible for results to agree with each other (be precise) and still be inaccurate.(See Figure 1)

Determinate errors have "assignable" causes which can usually be identified and either eliminated or controlled. (The terms "determinate" error, "assignable" error, and "systematic" error are synonymous).

A Sources of Determinate Error

1 Method error

Method errors are those that are inherent in the procedure. These are very serious and the hardest to detect and correct. The most common method error is the presence of interferences in the sample. Other examples would be precipitation of substances other than the desired material, partial solubility of precipitates, and entrainment as in a solvent extraction procedure.

2 Personal errors

Personal errors are attributable to individual mistakes which are consistently made by an analyst. These errors are the result of consistent carelessness, lack of knowledge or personal bias. Examples are errors in calculations, use of contaminated reagents, non-representative sampling, or poor calibration of standards and instruments.

3 Instrumental errors

Instrumental errors are those which are caused by an analytical instrument or by the effects of the environment acting on the instrument. Moisture in a G.C. column, improper wavelength markings on a spectrophotometer or incorrect scoring on a buret would be examples.

B Effects of Determinate Error

1 Additive

An additive determinate error is one which has a constant value regardless of the amount of analytically sought constituent present in the sample. (See Figure 2)

2 Proportional

A proportional determinate error changes value according to the amount of analytically sought constituent in the sample. (See Figure 3)

III DETECTION OF DETERMINATE ERROR

A Spiked Samples

1 Samples which can be determined before and after the addition of a known constituent (in the concentration range of interest) provide a way to detect determinate errors. Spiked samples should be representative and resemble actual conditions as closely as possible. The quantitation of bias can then be obtained with the following measures.

a Mean error - the difference between the mean of the data and the true result.

b Relative error - the mean error of a set of data expressed as a percentage of the true result.

EXAMPLE: An analyst determines the nitrate content of the effluent from his sewage treatment plant to be 0.50 mg/1. He then adds 1 mg/1 of standard nitrate solution to the sample. Table 1 shows the replicate results obtained on the spiked sample, and calculation of both mean and relative errors.

Table 1

Sample: Effluent
Determination: Nitrate (Modified Brucine)

Xi	
1.35	1.56
1.47	1.59
1.49	1.60
1.55	

1 Calculation of mean error

$$\bar{X} = \frac{10.61}{7} = 1.51 \text{ mg/1}$$

$$\text{Mean Error} = 1.51 - 1.50 = +0.01 \text{ mg/1}$$

2 Calculation of relative error

$$\% \text{ Relative Error} = \frac{+0.01 \times 100}{1.50} = +0.7\ \%$$

2 Control charts

Trends and shifts on control charts may also indicate determinant error. Using spiked samples, the standard deviation is calculated and control limits (usually ± 3 standard deviations) for the analysis are set (see Figure 4. For further discussion of control limits, see reference 3, p. 62.

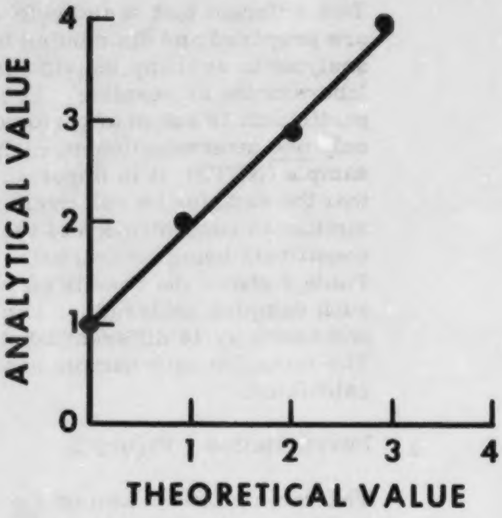


Figure 2. ADDITIVE ERROR

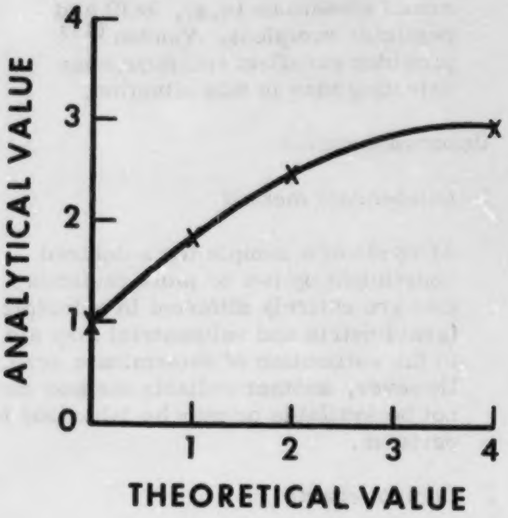


Figure 3. PROPORTIONAL ERROR

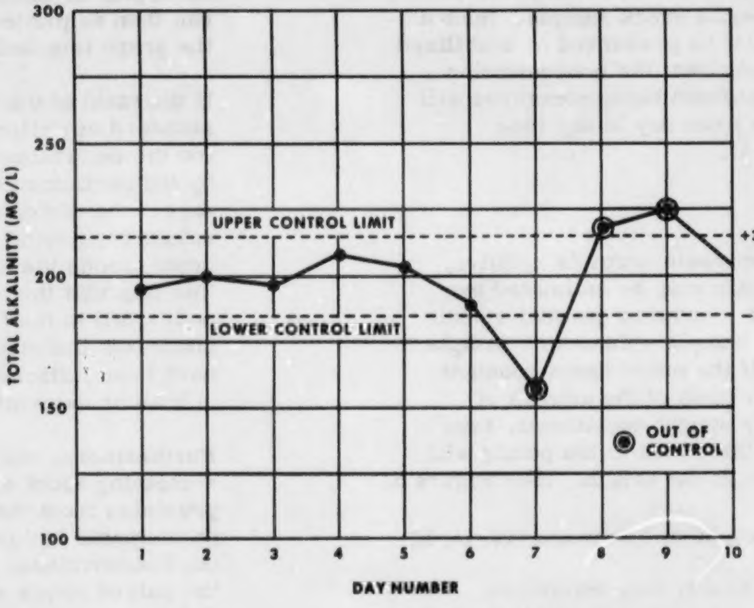


Figure 4. CONTROL CHART

3 In some cases, it is impossible to spike a sample so that it resembles actual conditions (e.g., BOD and pesticide samples). Youden (11) provides excellent techniques for detecting bias in this situation.

B Unknown Samples

1 Independent method

Analysis of a sample for a desired constituent by two or more methods that are entirely different in principle (gravimetric and volumetric) may aid in the estimation of determinate error. However, another reliable method may not be available or may be laborious to perform.

2 Control charts

It is possible to plot a control chart (Figure 4) even when it is not possible to spike a sample. One can use as a reference value an average of a series of replicate determinations performed on a composite check sample. Such a sample must be preserved or stabilized in such a way that the concentration of the constituent being measured will not change from day to day (see reference 1).

3 Aliquoting

If the determinate error is additive, the magnitude may be estimated by plotting the measured quantity versus a range of sample volumes or sample weights. If the error has a constant value regardless of the amount of analytically sought constituent, then a straight line fitted to the points will not go through the origin. (See Figure 5)

C Youden's Graphical Technique (10, 11, 12)

Dr. W. J. Youden has devised an approach to test for determinant errors with a minimum of effort on the part of the analyst and his laboratory. Samples used may be of known (spiked) or unknown composition.

1 Technique

Two different test samples (X and Y) are prepared and distributed for analysis to as many individuals or laboratories as possible. Each participant is asked to perform only one determination on each sample (NOTE: It is important that the samples be relatively similar in concentration of the constituent being measured). Table 2 shows the results on two such samples analyzed for percent potassium by 14 different laboratories. The mean for each sample has been calculated.

2 Interpretation - Figure 6

The vertical line drawn on the graph represents the mean ($\overline{X}$) of all the results obtained on Sample X; the horizontal line was drawn through the mean ($\overline{Y}$) of all the results obtained on sample Y. Each pair of laboratory results can then be plotted as a point on the graph (marked X. 1 etc.)

If the ratio of the bias (error) to standard deviation is close to zero for the determinations submitted by the participants, then one would expect the distribution of the paired values (or points) to be close to equal among the four quadrants. The fact that the majority of the points fall in the (+, +) and (-, -) quadrants indicates that the results have been influenced by some source of bias or determinate error.

Furthermore, one can even learn something about a participant's precision from the graph. If all participants had perfect precision (no indeterminate error), then all the paired points would fall on a 45° line passing through the origin. Consequently the distance from such a 45° line of each participant's point provides an indication of that participant's precision.

3. **Examples of Youden two-sample charts are in the Appendix (p4-13).**
4. **A quantitative treatment of this subject can be found in references 11 and 12.**

Table 2

Laboratory	Sample X	Sample Y
1	9.74%	8.50%
2	9.92	8.28
3	9.98	8.84
4	9.99	8.24
5	10.00	8.73
6	10.11	8.54
7	10.12	8.64
8	10.14	8.82
9	10.19	9.04
10	10.23	8.93
11	10.25	8.97
12	10.29	8.80
13	10.55	9.21
14	10.62	8.95

$\overline{X} = 10.15$ $\overline{Y} = 8.75$

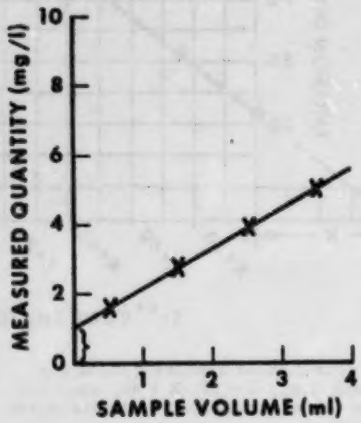


Figure 5

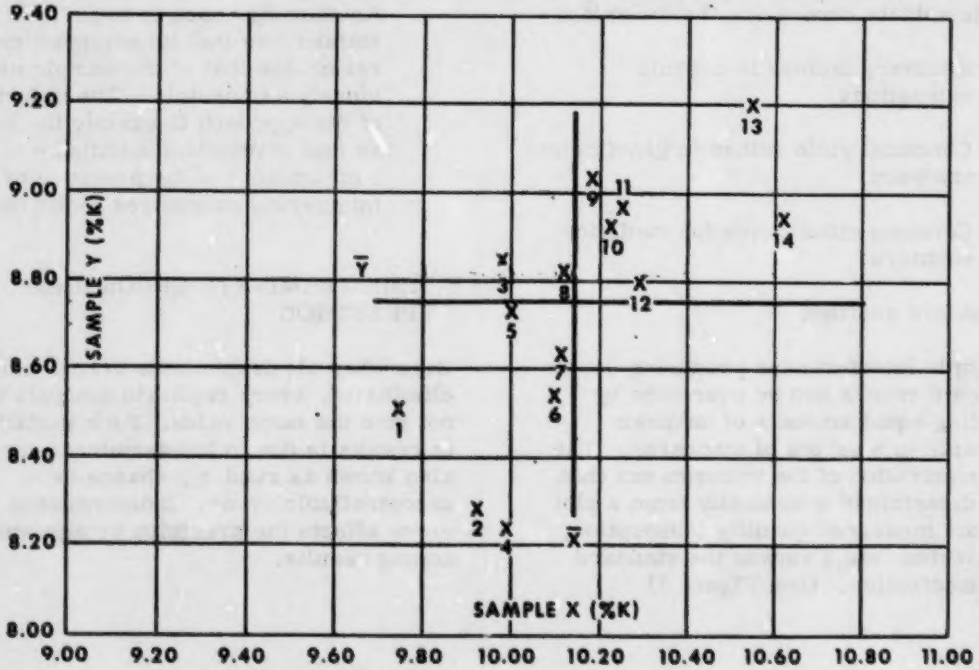


Figure 6. YOUDEN'S GRAPHICAL TECHNIQUE

IV ELIMINATION OF DETERMINATE ERROR

Various approaches can be used to eliminate the source of determinate error. The approach used depends upon whether the source is personal, method, or instrumental.

A Personal

Great care must be used to avoid producing an unconfident attitude in a technician. It is undesirable for the analyst to feel he is being "policed."

B Method and Instrumental

1 Blanks

Blanks can be used to correct for interferences from reagents, sample color, etc.

2 Correction factors

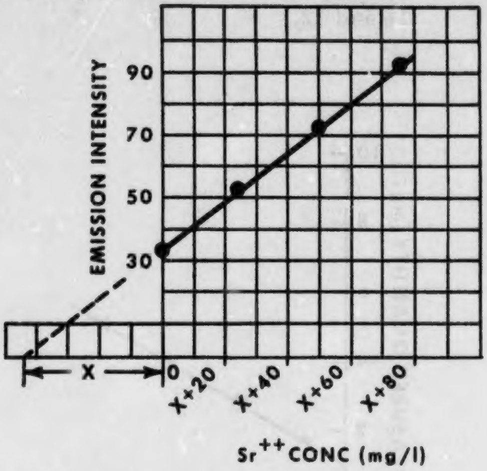
Examples of correction factors used in environmental analyses to eliminate determinate errors are the following:

- a Recovery factors in organic extractions
- b Chemical yield values in gravimetric analyses
- c Counting efficiencies for radiation counters

3 Standard addition

Sample interferences producing determinate errors can be overcome by adding equal amounts of unknown sample to a series of standards. The concentration of the unknown can then be determined graphically from a plot of the measured quantity (absorption, emission, etc.) versus the standard concentration. (See Figure 7)

Figure 7. METHOD OF STANDARD ADDITION GRAPHICAL METHOD OF COMPUTING Sr CONCENTRATION



NOTE: The X value appearing along the abscissa (i.e., X + 20, X + 40, etc.) refers to the unknown added to the strontium standard

4 Standard compensation

Another approach is to prepare the standard so that its composition resembles that of the sample as closely as possible. The objective of the approach is exactly the same as that of standard addition - to compensate for the presence of interfering substances in the unknown.

V INDETERMINATE ERROR AND PRECISION

Even when all determinate errors are eliminated, every replicate analysis will not give the same value. Such variation in results is due to indeterminate error, also known as random, chance or uncontrollable error. Indeterminate error affects the precision or agreement among results.

A Sources of Indeterminate Error

Indeterminate errors are due to unassignable or "chance causes." Examples are inadvertent contamination of sample or glassware, variation in reagent additions, or variations in instrument response (see Figure 8).

B Effects of Indeterminate Error

Since the causes of these errors are random, the effects are also random. Fortunately, these random variations conform to the "Laws of Chance" so statistical measures of precision can be used to quantitate indeterminate errors.

VI DETECTION OF INDETERMINATE ERROR

A measure of the degree of agreement among results can be obtained by analyzing a single sample repeatedly under a given set of conditions.

A Range

The range of the replicate results (difference between the lowest and the highest value) provides a measure of indeterminate variations.

B Standard Deviation

An estimation of indeterminate error can be obtained through a calculation of the standard deviation. The following formulas should be applied to random data which follows a normal distribution. Normality can be checked by ranking and plotting the data on normal probability paper; it should fall on a straight line (see Figure 9). Any values which do not fall close to the straight line (those values encircled) should be rejected in the calculation of standard deviation. Other statistical tests (8) can be used to objectively evaluate the rejection of outliers. The value obtained for standard deviation for a particular method may vary with the analyst, the concentration range of the constituent, and the composition of the sample analyzed. The confidence of the estimate is increased as the number of results (n) used to compute the standard deviation is increased.

1 Replicate results on the same sample:

$$s = \sqrt{\frac{\Sigma(X_i - \overline{X})^2}{n-1}} \qquad (1)$$

X_i = value of single result

$\overline{X}$ = average (mean) of results on same sample

n = number of results

Example: Table 3 contains a set of 5-day BOD results obtained on a synthetic sample containing 150 mg/l of glucose and 150 mg/l glutamic acid. (Note: A 1% dilution was used in the actual test). The results are those submitted by laboratories participating in a colaborative study. Calculate the standard deviation of these results.

$\overline{X}$ = 192 mg/l

n = 36.0

$\Sigma(X_i - \overline{X})^2$ = 58,200

$$s = \sqrt{\frac{58,200}{35}}$$

s = 41 mg/l

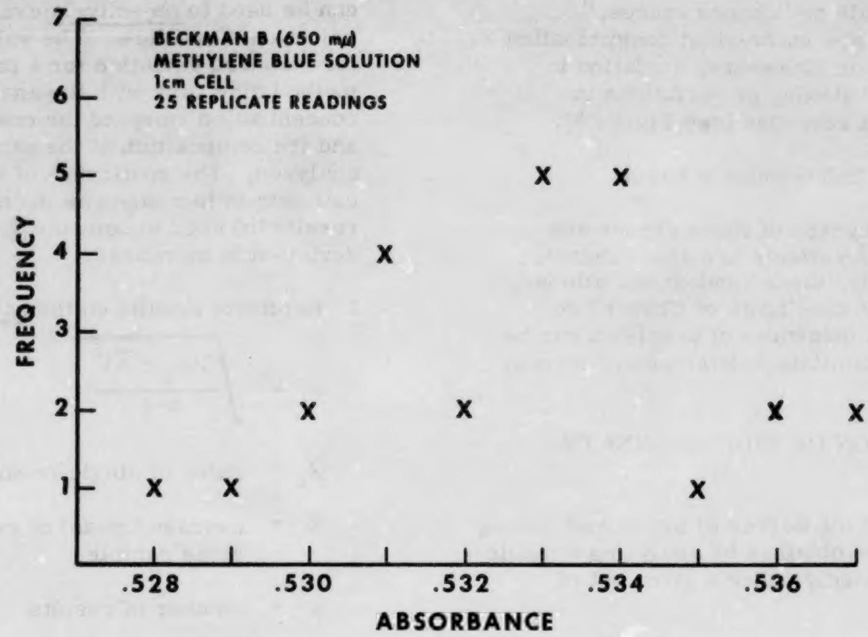


Figure 8. VARIATIONS IN SPECTROPHOTOMETER READINGS

FIGURE 9 NORMAL PROBABILITY CURVE

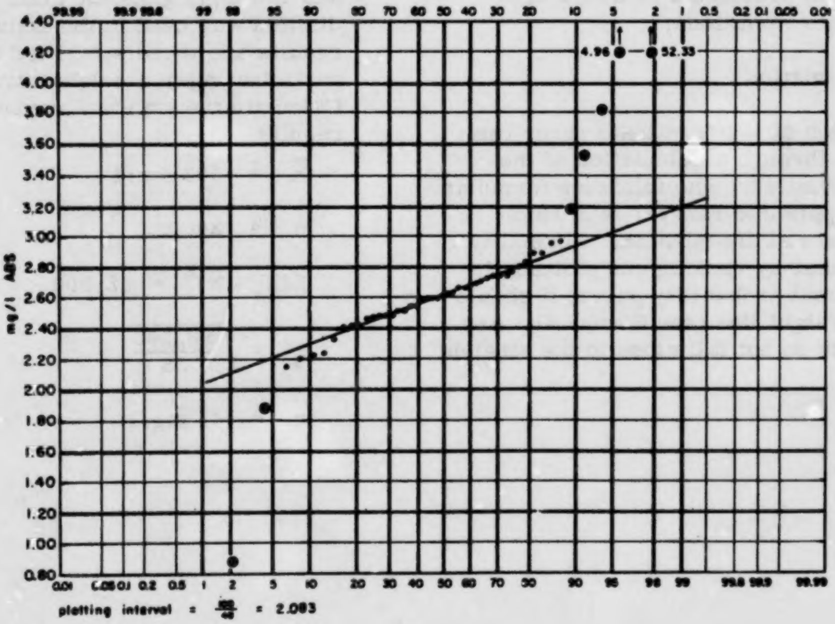


Table 3

SAMPLE: 150 mg/l glucose + 150 mg /l glutamic acid (1% dilution)
DETERMINATION: 5-day Biochemical Oxygen Demand

X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$	X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
100 mg/l	-92 mg/l	8464 $(mg/l)^2$	198 mg/l	6 mg/l	36 $(mg/l)^2$
117	-75	5625	199	7	49
125	-67	4489	200	8	64
132	-60	3600	200	8	64
142	-50	2500	204	12	144
147	-45	2025	210	18	326
153	-39	1521	211	19	361
160	-32	1024	212	20	400
165	-27	729	215	23	529
165	-27	729	223	31	961
167	-25	625	224	32	1024
173	-19	361	227	35	1225
178	-14	196	229	37	1369
189	- 3	9	238	46	2116
190	- 2	4	247	55	3025
196	4	16	250	58	3344
196	4	16	259	67	4489
197	5	25	274	82	6724

*Data taken from Water, Oxygen Demand Report (July, 1960), Analytical Reference Service, Training Program, R.A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

Table 4*

SAMPLE: Aqueous
CONCENTRATION RANGE: 30 - 70 mg/l
DETERMINATION: Phosphate (Lucerna, Conde, and Prat Method)

Sample	Mg/l P	d	d^2	Sample	Mg/l P	d	d^2
A	51 53	2	4	L	54 56	2	4
B	39 39	0	0	M	38 37	1	1
C	53 54	1	1	N	52 52	0	0
D	47 47	0	0	O	58 58	0	0
E	50 51	1	1	P	54 54	0	0
F	48 47	1	1	Q	54 54	0	0
G	50 50	0	0	R	48 48	0	0
H	47 47	0	0	S	52 51	1	1
I	42 42	0	0	T	53 53	0	0
J	50 51	1	1	U	46 47	1	1
K	59 60	1	1	V	42 42	0	0

*Data obtained from Frank Schickner, Proctor and Gamble Company.

2 Duplicate results on different samples

In a laboratory where duplicates are routinely run, it would be simple to use the following formula for evaluation of standard deviation.

$$s = \sqrt{\frac{\Sigma(d^2)}{2k}} \quad \text{(See reference 5, page 654)} \qquad (2)$$

d = difference between duplicates

k = number of samples

Example: Table 4 contains a set of phosphate results obtained on aqueous samples in the range 100-200 mg/l. Calculate the standard deviation of these results.

$$\Sigma(d^2) = 16$$

$$k = 22$$

$$s = \sqrt{\frac{16}{44}}$$

$$s = .61 \text{ mg/l}$$

3 Duplicate and triplicate results on different samples

$$s = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n - k}} \quad \text{(See reference 7, page 73)} \qquad (3)$$

$\bar{x}$ = average of results on the same sample
n = total number of results
k = number of different samples

Example: Table 5 contains a set of % nitrogen results obtained on unknown organic compounds.

Calculate the standard deviation.

$$\Sigma(X_i - \bar{X})^2 = .2401$$

$$n - k = 22$$

$$s = \sqrt{\frac{.2401}{22}}$$

$$s = .104\%$$

4 Use of range to estimate standard deviation

For a small number of replicates ($n < 10$), the range can be used to estimate the standard deviation (See Table 6).

$$\frac{R}{d_N} = s \qquad (4)$$

Example: Table 7 contains a set of replicate nitrate results. Calculate the standard deviation of these results.

a Use of formula (1)

$$\bar{X} = 0.72 \text{ mg/l}$$

$$n = 5$$

$$\Sigma(X_i - \bar{X})^2 = .0134$$

$$s = \sqrt{\frac{.0134}{4}}$$

$$s = .058 \text{ mg/l}$$

b Use of formula (4)

$$R = .14 \text{ mg/l}$$

$$d_N = 2.33$$

$$s = \frac{.14 \text{ mg/l}}{2.33}$$

$$s = .060 \text{ mg/l}$$

C Coefficient of Variation

An estimation of indeterminate error can also be made by calculating the coefficient of variation (V), also known as % relative standard deviation:

$$V = \frac{s}{\bar{X}} \times 100$$

By comparing the standard deviation (dispersion) to the average or mean value (central tendency) in a set of data and expressing this relative standard deviation as a percentage, the analyst has a meaningful interpretation of the degree of dispersion present. Indeter-

Table 5*

SAMPLE: Unknown Organic Compounds
DETERMINATION: % Nitrogen (Kjeldahl)

CONCENTRATION
RANGE: 10% - 20%

Sample	%N	$\bar{X}$	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
A	16.48	16.47	.01	.0001
	16.46		.01	.0001
B	16.50	16.50	0	0
	16.49		.01	.0001
C	16.72	16.65	.07	.0049
	16.57		.08	.0064
D	17.52	17.58	.06	.0036
	17.60		.02	.0004
	17.63		.05	.0025
E	16.31	16.31	0	0
	16.30		.01	.0001
F	16.40	16.35	.05	.0025
	16.31		.04	.0016
	16.35		0	0
G	17.56	17.55	.01	.0001
	17.54		.01	.0001
H	14.96	14.81	.15	.0225
	14.66		.15	.0225
I	19.15	19.02	.13	.0169
	18.89		.13	.0169
J	13.93	13.75	.18	.0324
	13.56		.19	.0361
K	10.34	10.27	.07	.0049
	10.19		.08	.0064
L	17.16	17.15	.01	.0001
	17.13		.02	.0004
M	15.01	15.03	.02	.0004
	15.05		.02	.0004
N	12.44	12.62	.18	.0324
	12.70		.08	.0064
	12.73		.11	.0121
O	14.37	14.37	0	0
	14.36		.01	.0001
P	11.85	11.85	0	0
	11.85		0	0
Q	14.79	14.73	.06	.0036
	14.70		.03	.0009
	14.70		.03	.0009
R	17.19	17.17	.02	.0004
	17.14		.03	.0009

*Data obtained from Frank Schickner, Proctor and Gamble Company.

Table 6*

FACTORS USED TO ESTIMATE THE STANDARD DEVIATION FROM RANGE

Size of Sample (n)	d_N	$\frac{1}{d_N}$
2	1.13	.887
3	1.69	.591
4	2.06	.486
5	2.33	.430
6	2.53	.395
7	2.70	.370
8	2.85	.351
9	2.97	.337
10	3.08	.325

*Natrella, Experimental Statistics,(8) pp. 2-6.

Table 7

SAMPLE: Ohio River Water

DETERMINATION: Nitrate (Modified Brucine)

X_1	$X_1 - \bar{X}$	$(X_1 - \bar{X})^2$
0.65 mg/lN	-0.07	.0049
0.68	-0.04	.0016
0.70	-0.02	.0004
0.76	+0.04	.0016
0.79	+0.07	.0049

minate error wouldbe the cause of undue dispersion.

Example: Table 3

$s = 41$ mg/l

$\overline{X} = 192$ mg/l

$V = \frac{41}{192} \times 100$

$V = 21\%$

D An indication of an individual's analytical precision can be obtained by his participation in an interlaboratory study. In this case, the analyst performs only one determination on each of two samples. Using Youden's Graphical Technique as an indication of an individual's precision was discussed previously in this outline in III C.

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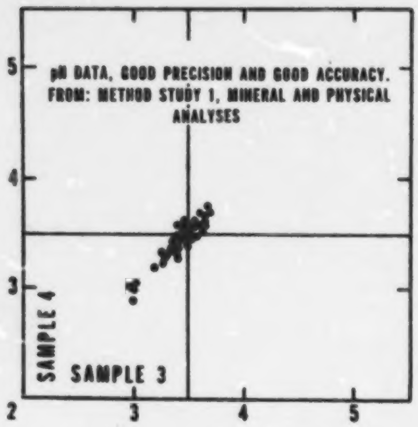
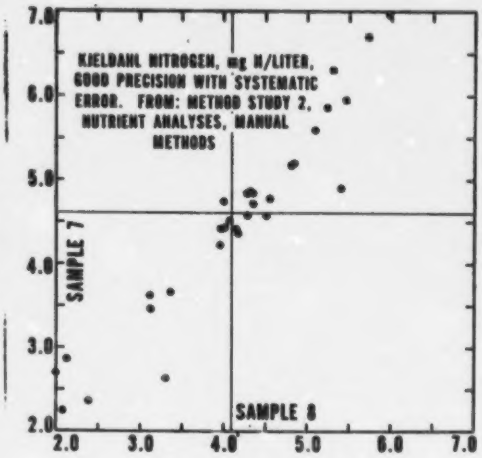
This outline was prepared by Betty A. Punghorst, former Chemist, National Training Center, and revised by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Accuracy, Data Collections, Data Processing, Error Analysis, Errors, Graphic Methods, Measurement, Monitoring, Precision, Quality Control

APPENDIX


pH DATA, GOOD PRECISION AND GOOD ACCURACY. FROM: METHOD STUDY 1, MINERAL AND PHYSICAL ANALYSES
SAMPLE 4
SAMPLE 3
5
4
3
2
3
4
5


KJELDAHL NITROGEN, mg N/LITER, GOOD PRECISION WITH SYSTEMATIC ERROR. FROM: METHOD STUDY 2, NUTRIENT ANALYSES, MANUAL METHODS
SAMPLE 7
SAMPLE 8
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4.0
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2.0
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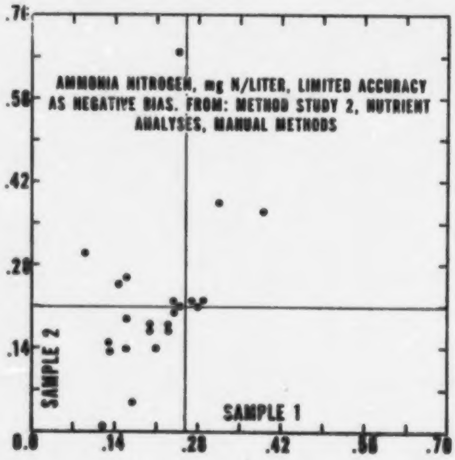
4.0
5.0
6.0
7.0


AMMONIA NITROGEN, mg N/LITER, LIMITED ACCURACY AS NEGATIVE BIAS. FROM: METHOD STUDY 2, NUTRIENT ANALYSES, MANUAL METHODS
SAMPLE 2
SAMPLE 1
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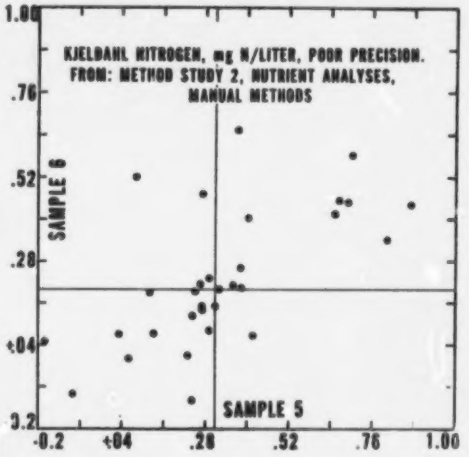
.42
.28
.14
0.0
.14
.28
.42
.56
.70


KJELDAHL NITROGEN, mg N/LITER, POOR PRECISION. FROM: METHOD STUDY 2, NUTRIENT ANALYSES, MANUAL METHODS
SAMPLE 6
SAMPLE 5
1.00
.76
.52
.28
+.04
-0.2
-0.2
+.04
.28
.52
.76
1.00

ELEMENTS OF A QUALITY ASSURANCE PROGRAM

I WATER QUALITY DATA

A Importance

- 1 Criteria for decisions
  - a Planning
  - b Permit issuance
  - c Compliance
  - d Enforcement
  - e Evaluation of treatment processes
  - f Research decisions
- 2 Effects of decisions
  - a Social
  - b Legal
  - c Economic

B Requirements for Reliability

- 1 Specificity
- 2 Accuracy
- 3 Precision

C Elements of Quality Assurance(1)

- 1 Valid sample
- 2 Recognized methodology
- 3 Control of services, instruments, equipment and supplies
- 4 Quality analytical performance
- 5 Efficient data handling and reporting

D Documentation System

- 1 Complete and permanent records must be kept by all field and laboratory personnel.
- 2 Any procedures undertaken as quality checks should also be recorded, dated and signed.
- 3 The results of any quality checks should be recorded, dated and signed.
- 4 Any checks by outside service personnel should be recorded, dated, and signed.

E Quality Assurance Control Coordinator(2)

- 1 Overall responsibility for program: development, implementation, administration
- 2 Continuing assessment of level of operations
- 3 Identification of training needs and provision to accomplish
- 4 Coordinator for inter-laboratory quality control programs

II SAMPLE

A Validity(3, 4, 5, 6)

- 1 Representative
- 2 Properly collected
- 3 Clean, appropriate containers
- 4 Approved preservation measures
- 5 Analytical checks on containers and preservatives
- 6 Holding times observed

B Integrity(2, 7)

1 Written procedures for all aspects of sample handling

2 Field labels, records, seal

3 Appropriate transport to laboratory

4 Logging in system

5 Appropriate storage conditions and holding time

6 System for distribution for analysis

7 System for storage or discard

8 System for chain-of-custody documentation

III RECOGNIZED METHODOLOGY

A Need for Standardization

1 Within one laboratory

2 Between cooperating laboratories

3 Users of common data bank

4 Nation-wide requirements

B Criteria for Selection(6)

1 Specificity with accuracy and precision

2 Validity established by sufficient use and evaluation

3 Equipment and skill requirements normally available

4 Time requirement reasonable

C Sources

1 Annual Book of ASTM Standards(3)

2 Standard Methods for the Examination of Water and Wastewater(5)

3 Methods for Chemical Analysis of Water and Wastes (6)

4 U.S. Geological Survey Techniques of Water Resources Inventory(8)

5 Others

D Commonly-Used Types(9)

1 Various sample treatments (filtration, digestion, etc.)

2 Electrode-meters

3 General analytical methods

a Volumetric analysis

b Gravimetric procedures

c Combustion

4 Photometric methods

a Atomic absorption

b Flame emission

c Colorimetry

5 Gas chromatography

E Selection on Basis of Use of Data

1 Compliance monitoring

a National Pollutant Discharge Elimination System and State Certifications(10)

1) Use of alternate procedures

2) Procedures for non-listed parameters

b National Interim Primary Drinking Water Regulations(11)

1) Use of alternate procedures

2) Procedures for non-listed parameters

2 State monitoring programs(12)

  a Fixed station ambient monitoring

  b Intensive survey programs

3 Local regulations

4 Pre-survey field investigations

5 Control of treatment processes

F Using Recognized Procedures

1 Written step-by-step laboratory manuals

2 Strict adherence to reference source

3 Record of modifications and why

G Field Kits

1 Shortcomings

2 Uses

IV CONTROL OF SERVICES, INSTRUMENTS, EQUIPMENT AND SUPPLIES(1)

A Services

1 Distilled water

  a Ammonia-free

  b Carbon dioxide-free

  c Ion-free

  d Low organic background

2 Compressed air

  a Dry

  b Oil-free

  c No contaminants

3 Electrical service

  a Adequate voltage

  b Constant voltage

  c Appropriate grounding

  d Efficient lighting

B Instruments

Applicable to laboratory and field instruments; and, as possible, fixed continuous monitoring devices.

1 Written requirements for daily warm up, standardization, calibration, and/or optimization procedures.

2 Standards available to perform daily check procedures. Some examples:

  a Standardized weights

  b Certified thermometer

  c Filter (or solution) for wavelength alignment check

  d Standard reference materials with standard absorption curves

  e Standard resistor

  f Calibration solutions (buffers, conductivity or turbidity standards)

  g Parameter standards to establish or to check calibration curves

  h Radioactive standards with date and count

3 Written trouble-shooting procedures

4 Schedule for required replacement or cleaning procedures

5 Schedule for check and/or adjustments by service personnel

C Laboratory Equipment

- 1 Great variety
  - a Of materials (glass, plastic, porcelain, etc.)
  - b Of grades
  - c Of accuracy in calibration
  - d Of specific properties
  - e Of unique construction
- 2 Selection depends on function
  - a Measurement and delivery of volumes require varying degrees of accuracy.
  - b Storage of reagents and solutions necessitates composition considerations such as:
    - 1) Polyethylene bottles for solutions of boron, silica and alkali
    - 2) Glass containers for organics
    - 3) Brown glass for light-sensitive solutions
  - c Confinement of reactions may present special requirements such as·
    - 1) Ground glass joints
    - 2) Teflon plugs
    - 3) Special resistance to thermal shock
    - 4) Impervious to digestion conditions
  - d Volumetric analyses involve:
    - 1) Very accurately calibrated glassware
    - 2) Consideration of the temperature at which the apparatus was calibrated
  - e Other laboratory operations like filtration, ion exchange, absorption and extractions may require specialized construction like fritted ware which has pressure and thermal shock limits.
- 3 Cleaning procedures
  - a Basis of selection
    - 1) Appropriate for the composition material
    - 2) Appropriate for materials to be removed
    - 3) Appropriate for subsequent use - (Avoid introducing contaminants)
  - b Definite program
    - 1) Standardized, consistent, mandatory
    - 2) Analytical checks on effectiveness

D Laboratory Supplies - Reagents, Solvents and Gases(1)

- 1 Required purity depends on:
  - a What is measured
  - b Sensitivity of method
  - c Specificity of detection system
- 2 General guides

  If purity is not specified in the method, some general guides are:
  - a General inorganic analyses
    - 1) Analytical reagent (AR) grade chemicals, except use primary standard grade for standardizing solutions.
    - 2) Distilled water and solvents free of constituent
    - 3) Commercial grade gases

b Metals analyses by flame

1) Spectroquality chemicals for standards

2) Spectroquality recommended for other reagents and solvents, though analytical reagent grade may be satisfactory.

3) Acids should be distilled in glass

4) Deionized distilled water

5) Commercial grade or laboratory-supplied gases

c Radiological analyses

1) Scintillation grade reagents and solvents

2) High purity, extra dry gases with low radioactive background

d Organic analyses

1) Reference grade when available, AR at minimum

2) For gas chromatography (GC), various detectors require absence of certain classes of compounds, and may necessitate treatment of chemicals.

3) Pesticide quality solvents For GC, check assay.

4) Type of detector affects gas quality required. Molecular-sieve carrier-gas filters and drying tubes are required on combustion gases.

3 Program for assuring quality

a Written purity requirements according to methods utilized

b Date all on receipt.

c Observe shelf life recommendations. Dicard date on container.

d Observe appropriate storage requirements.

e Check assay for possible interferences.

f Run reagent and solvent blanks.

g As applicable, check background of reagents and solvents.

h Run method blanks (all reagents and solvents) with every series of samples or one for every nine samples.

i Definite procedures for limits of error, clean-up procedures or application of correction factors

j Replace gas cylinders at 100-200 psi.

4 Procedures for removing impurities

a Recrystallization

b Precipitation

c Distillation

d Washing with solvent(s) used in analysis

e Aging (gases)

f Others

5 Reagent and standard solutions

a Preparation

1) Use of primary standard grade chemicals as required

2) Careful weighing

3) Class A volumetric glassware

4) Appropriate quality distilled water or solvent

5) Label listing compound(s), concentration, date of preparation or discard, preparer

6) Very dilute standards prepared at time of use

b Standardization as appropriate

1) Use reliable primary standards,

2) Restandardize as required by stability.

c Purchased solutions

1) Should contain chemicals specified by method

2) Should be checked for accuracy

d Storage

1) Clean containers of material suitable for solution to be stored

2) Tight-fitting stoppers or caps

3) Safeguards against evaporation of solvent, adsorption of gases and water vapor, effects of light or temperature, etc.

e Signs of deterioration

1) Discoloration

2) Formation of precipitates

3) Significant change in concentration

V QUALITY ANALYTICAL PERFORMANCE(1)

A Skilled Analyst

1 Appropriate and continuing training

2 Willingness to follow specified procedures

3 Skilled in manipulation of laboratory equipment and techniques required in analyses

4 Understanding of basic principles utilized and design of any instruments s/he uses.

5 Knowledgeable and skilled in performing the analyses for which responsible

6 Precision and accuracy performance acceptable

B Establishing Analyst Precision

Applicable except for gas chromatography and radiological instrumentation.

1 Seven replicates of four samples covering the concentration range of applicability for analysis

2 Test among routine samples over two hours or more in normal operating conditions.

3 Calculate the standard deviation for each set.

4 Compare result to precision statement for method in the source of the procedure. (It may be stated as % relative standard deviation. If so, calculate analyst results in this form).

5 Individual's precision should be better than round-robin precision results.

C Establishing Analyst Accuracy

Exceptions: gas chromatography and radiological instrumentation

1 Spike set of 7 precision replicates of concentration low in applicability range to bring final to twice original.

2 Spike set of 7 precision replicates of mid-range concentration to bring final to about 75% of upper limit of applicability.

3 Test among routine samples over two hours or more in normal operating conditions.

4 Calculate % recovery for each set using average of results from the precision check and the recorded spike amounts.

5 Compare result to accuracy statement for method in the source of the procedure. (It may be stated as % bias, i.e., % recovery-100%).

6 Individual's accuracy should be better than round-robin accuracy results.

D Daily Performance Evaluation

1 At least two standards (high and low) analyzed with a blank to verify an established standard curve (comparable operating conditions).

2 Some methods require daily preparation of a standard curve.

3 One of about every 10 samples should be a duplicate to check precision according to acceptable standard deviation (or % relative std. deviation).

4 One of about every 10 samples should be a spiked sample to check accuracy according to acceptable % recovery (or % bias).

E Documentation of Daily Performance

1 After 20 sets of duplicate data results or of spiked sample results have been collected, control charts for precision and accuracy, respectively, can be constructed.

2 A variety of construction methods is available.

3 Plot succeeding results on the appropriate chart.

4 Charts document reliability of data.

5 Charts give signal of out-of-control numbers, trends toward out-of-control conditions, improved performance, etc.

F Interlaboratory Checks on Performance(2)

1 Quality Control samples for many constituents are available from EPA at no charge through EPA Regional Quality Assurance Coordinators. The concentration is provided with the sample. These might be run every three to six months.

2 Run split samples and compare results with the other laboratory.

3 Run performance samples (unknowns) available from EPA at no charge.

4 Participate in round-robin method and performance evaluation studies.

5 Participate in laboratory evaluation programs.

VI DATA HANDLING AND REPORTING(1)

A laboratory must have a program for systematic and uniform recording of data, and for processing and reporting it in proper form for interpretation and use.

A The Analytical Value

1 Correct calculation formulas reduced to simplest factors for quick, correct calculations.

2 Provisions for cross-checking calculations

3 Rounding-off rules uniformly applied

4 Significant figures established for each analysis

B Processing

1 Determine control chart approach and statistical calculations required for quality assurance and report purposes.

2 Develop report forms to provide complete data documentation and permanent records, and also to facilitate data processing.

a To avoid copying errors, the number of forms should be minimal.

C Reporting

The program for data handling should provide data in the form/units required for reporting.

D Storage

1 For some types of data, laboratory records must be kept readily available to regulatory agencies for a period of time.

2 A bound notebook or preprinted data forms permanently bound provide good documentation.

3 STORET is a system for storage and retrieval of water quality data. It is a State/Federal cooperative activity which provides States with direct access into the central computer system.

4 Many agencies have access to local systems for storage and retrieval of data.

VII SAFETY CONSIDERATIONS[13]

A Laboratory Facilities

B Emergency Equipment

C Program for Health Checks as Required

D Program for Inventory and Control of Toxic and Hazardous Materials and Test Wastes

E Safety Officer-Responsibilities

1 Information

2 Planning

3 Inspection

4 Implementation

5 Evaluation

6 Reports

VIII EPA Regional QA Coordinators

A Each of the ten EPA Regions has a Quality Assurance Coordinator.

1 Implements program in regional laboratory

2 Maintains relations and serves as source of information for state and interstate agencies within the region

3 Serves as liason for EPA's Environmental Monitoring and Support Laboratory (EMSL).

B The name, address and telephone number of the regional QA Coordinator can be obtained from the EPA Regional Administrator's Office or from EPA-EMSL, Cincinnati, Ohio 45268.

IX SUMMARY

Quality Assurance regarding water quality (or any type of) laboratory data requires planning, control and checking for every phase of the operation from sample collection through storage of the data. This outline contains a basic checklist of information and items to be considered when developing a program to facilitate quality analytical performance by laboratory personnel.

To make the program effective, procedures must be written, responsibilities must be clearly defined and assigned, and individuals must be accountable. Development and daily performance of such a program which meets the needs of an individual laboratory (or agency) will take time. Considering the importance of the data produced, the investment in assuring its reliability is a sound one.

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DESCRIPTORS: Analytical Techniques, Chemical Analyses, Quality Assurance, Quality Control, Reliability, Water Analysis

VOLUMETRIC ANALYSIS OF WATER QUALITY

I INTRODUCTION

A A standard solution is one whose composition and concentration are known to a high degree of accuracy. In chemical analyses, it is used to determine the concentration of a particular component in a sample.

B These chemical analyses very frequently involve an acid-base reaction or an oxidation-reduction reaction.

C Three important terms connected with these two types of chemical reactions are: mole, equivalent weight, and normality. These terms will be defined in following sections.

II ANALYTICAL CHEMICAL REACTIONS

A As stated above, in a chemical analysis a volume of standard solution is brought into contact with a volume of sample in order to determine the concentration of some particular component of the sample.

B For a given volume of sample, it is necessary to use a definite amount of the standard solution--too much or too little would give erroneous results.

C For example, one cannot simply mix together random volumes of sodium hydroxide and hydrochloric acid solutions and expect the only two substances produced to be sodium chloride and water.

D Unless the concentrations of the two reagents are known and the amounts measured accurately, excess sodium hydroxide or hydrochloric acid will also remain at the end of the reaction.

E The reason for these limitations is that when molecules react with one another, they do so in definite ratio. Unless the number of molecules of each reactant is known, there will always be an excess of one of the reactants remaining at the end of the chemical reaction. As mentioned before, this leads to erroneous analytical results.

F Because of their size, it is not possible to count out numbers of molecules. However, the number of molecules in a quantity of a chemical may be found by determining its weight and consulting a table which lists the weights of the atoms making up the chemical.

G For example, sodium hydroxide has the formula NaOH. It can also be stated that a molecule of sodium hydroxide consists of one sodium atom, one hydrogen atom and one oxygen atom.

One sodium atom weighs 23 atomic mass units (amu). An oxygen atom weighs 16 amu; and a hydrogen atom weighs 1 amu.

A molecule of sodium hydroxide, therefore, weighs 40 amu; all amu values have been rounded off. Forty amu is the molecular weight of sodium hydroxide.

H A mole of any chemical is a number of grams numerically equal to the molecular weight of that chemical. One mole of sodium hydroxide, therefore, contains 40 grams (40 g).

I Similarly, the atomic weight of a chlorine atom is 35 amu; that of a hydrogen atom is 1 amu; and the molecular weight of the hydrogen chloride molecule is 36 amu. One mole of hydrogen chloride weighs 36 g.

J Synonyms for mole are: mol, gram mol, gram mole, and gram molecular weight.

K Tables listing atomic weights of the elements can be found in virtually all of the texts used for high school and first year college chemistry courses.

L The remaining two terms mentioned in I C (equivalent weight and normality) will be considered as they are related to acid-base and oxidation-reduction reactions.

III ACID-BASE REACTIONS

A Recall that an acid is a substance which donates a hydrogen ion, or proton, (H^+) in a chemical reaction and a base is a substance which donates a hydroxide ion (OH^-) or accepts a proton in a chemical reaction. Reactions involving these processes are called acid-base reactions.

B In the case of sodium hydroxide, the molecular weight is 40 amu and one mole of sodium hydroxide weighs 40 g. One hydroxide ion is contained in the sodium hydroxide molecule.

1 For a base, the number of grams in a mole divided by the number of hydroxide ions equals a quantity called the equivalent weight. Examples are given below. All amu values have been rounded off.

a Base - potassium hydroxide KOH

Atoms	Number	Wt/atom	Total
K	1	39 amu	39 amu
O	1	16	16
H	1	1	1
			56 amu

One mole of KOH = 56 g
Number of hydroxide ions = 1
Equivalent weight of KOH = 56 g

b Base - calcium carbonate $CaCO_3$

Atoms	Number	Wt/atom	Total
Ca	1	40 amu	40 amu
C	1	12	12
O	3	16	48
			100 amu

One mole $CaCO_3$ = 100g
Number of protons (H^+) it can accept = 2
Equivalent weight of $CaCO_3$ = 50g

2 For an acid, the number of grams in a mole divided by the number of hydrogen ions is the equivalent weight. Examples are given below. All amu values have been rounded off.

a Acid - nitric acid HNO_3

Atoms	Number	Wt/atom	Total
H	1	1 amu	1 amu
N	1	14	14
O	3	16	48
			63 amu

One mole of HNO_3 = 63 g
Number of hydrogen ions = 1
Equivalent weight of HNO_3 = 63 g

b Acid - sulfuric acid H_2SO_4

Atoms	Number	Wt/atom	Total
H	2	1 amu	2 amu
S	1	32	32
O	4	16	64
			98 amu

One mole of H_2SO_4 = 98 g
Number of hydrogen ions = 2
Equivalent weight of H_2SO_4 = 49 g

C Normality is a method of expressing solution concentrations. If one equivalent weight of a chemical is dissolved in a solvent and the volume brought to one liter (l), the concentration of the solution is one normal (N).

1 The equivalent weight of KOH was calculated to be 56 g. This amount of the solid dissolved in water and diluted to a liter would give a 1 N solution.

2 The equivalent weight of HNO_3 was found to be 63 g. This quantity of acid diluted to a liter would give a 1 N solution.

IV OXIDATION-REDUCTION REACTIONS

A The concepts of mole, equivalent weight and normality, as described in previous sections, apply also to oxidation-reduction reactions.

B One definition of an oxidation is that it involves an increase in the oxidation state (charge) of an atom.

For example: $FeCl_2 \rightarrow FeCl_3$. In this conversion the Fe has been oxidized from +2 to +3.

C A reduction is a decrease in the oxidation state (charge) of an atom.

For example: $KMnO_4 \rightarrow MnO_2$. In this conversion the Mn has been reduced from +7 to +4.

D The equivalent weight of an oxidizing or reducing agent is calculated by dividing the number of grams in a mole of the reagent by the change in charge involved.

For example: $FeCl_2$ (used as a reducing agent).

Atoms	Number	Wt/atom	Total
Fe	1	56 amu	56 amu
Cl	2	70	70
			126 amu

One mole of $FeCl_2$ = 126 g
Change in charge = 1
Equivalent weight of $FeCl_2$ = 126 g

The concentration of a liter of solution which contains 126 g of $FeCl_2$ is 1 N.

V VOLUMETRIC ANALYSIS

Volumetric analysis involves a titration which is the process of determining the strength or concentration of an accurately measured volume of sample by reacting it with an accurately measured volume of a standard solution.

A Chemical Reactions

Chemical reactions take place during the titration. Acid-base reactions and oxidation-reduction (redox) reactions are commonly utilized in water quality titrations.

B Complete Reactions

All of the sample component of interest must react in order to quantitatively determine its concentration. You need some indicator of when the reaction is complete. Two types of indicators are those you can detect visually (e.g. appearance of a color) or by a change in an electrical property (e.g. amperage) when the reaction is completed.

C Volumes

The volume of sample and of the reacting standard solution must be measured very accurately.

1 Sample - The sample is measured into the titration vessel. Ordinarily, a pipet is used for the measurement unless the volume exceeds 100 ml.

2 Standard Solution - A buret is used to measure the standard solution required to complete the reaction.

D Concentrations

1 The concentration of the standard solution is expressed either in moles per liter (molarity) or in equivalent weights per liter (normality). A detailed discussion about calculating moles and equivalent weights can be found in III and IV above.

2 Sample - The concentration of the constituent of interest in the sample is determined by calculation (next).

E Calculations

1 The basic relationship utilized in these calculations is:

(Normality) (Volume) of the sample equals (Normality) (Volume) of the standard solution.

At the end of a titration, three of the four factors are known so it is very easy to calculate the one unknown:

$$(1)\ N \text{ of sample} = \frac{(N \times V) \text{ of standard}}{V \text{ of sample}}$$

2 Normality expresses the number of equivalent weights of the constituent present in the sample. To convert normality to an expression of weight, this relationship applies:

$$(2)\ \text{grams} = (\text{No. Eq. Wts})(\text{Eq. Wt.})$$

3 Since N of sample equals the No. Eq. Wts, we can substitute formula (1) for (No. Eq. Wts.) in formula (2) above to yield this calculation formula for g of sample:

$$(3)\ g = \frac{[(N \times V) \text{ of standard}]\ (\text{Eq. Wt.})}{V \text{ of sample}}$$

4 To express the weight of the constituent as a concentration on a per liter basis, another factor is added to the combined formula (3) to give the final calculation formula:

$$(4)\ g = \frac{[(N \times V) \text{ of standard}]\ (\text{Eq. Wt.})\ (1000)}{V \text{ of sample}}$$

Where V is in liter units and Eq. Wt. is in grams.

The formula can be used to find mg if V is in ml units and the Eq. Wt. is expressed in mg.

5 An example of the application of the formula to express the results of an alkalinity titration would be:

$$\text{mg/L } CaCO_3 = \frac{(\text{Vol std})(\text{Nstd}) \times 50 \times 1000}{\text{ml sample}}$$

where:

Vol std - the volume of a standard solution of acid measured by a buret during the titration.

N std - The standard acid used is known to be a certain normality

50 - equivalent weight of $CaCO_3$

1000 - result is to be expressed as a per liter concentration

ml sample - measured at beginning of titration

VI PRIMARY STANDARDS

A A reagent of known purity is called a primary standard. Primary standard grade chemicals are available from chemical supply houses and the National Bureau of Standards. An accurately measured quantity of a primary standard is used for the preparation of standard solutions.

B Other requirements of a primary standare are:

1 It must be stable at 105° C (the temperature used for drying).

2 It should not be reactive with components of the air, such as O_2 and CO_2.

3 It should have a high equivalent weight so as to minimize any errors in the analysis.

4 It should be readily available at a reasonable cost.

VII STORAGE OF STANDARD SOLUTIONS

A Standard solutions should be prepared using high quality distilled water.

B Care should be taken to insure the cleanliness of the glass or plastic bottle used for storage.

C Some solutions may decompose on exposure to light and should be stored in dark bottles.

D The stopper or cap should fit tightly.

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Descriptors: Analytical Techniques, Chemical Analysis, Volumetric Analysis, Water Analysis

ACIDITY, ALKALINITY, pH AND BUFFERS

I DEFINITIONS OF ACIDS AND BASES

A Arrhenius Theory of Acids and Bases (Developed about 1887)

1 Acid: A substance which produces, in aqueous solution, a hydrogen ion (proton), H^+.

2 Base: A substance which produces, in aqueous solution, a hydroxide ion, OH^-.

3 The Arrhenius theory was confined to the use of water as a solvent.

B Bronsted and Lowry Theory of Acids and Bases (Developed about 1923)

1 Acid: A substance which donates, in chemical reaction, a hydrogen ion (proton).

2 Base: A substance which accepts, in chemical reaction, a hydrogen ion (proton).

3 Bronsted and Lowry had expanded the acid-base concept into non-aqueous media; i.e., the solvent could, but didnot have to be,water.

C There are other acid-base theories. The two above are probably the most commonly used ones when discussing wastewater topics however.

II DEFINITIONS OF ACIDITY, ALKALINITY AND NEUTRALITY

A Acidity of a Water:

Its quantitative capacity to neutralize a strong base to a designated pH.

B Alkalinity of a Water:

Its quantitative capacity to neutralize a strong acid to a designated pH.

C Neutrality

1 It is possible to have present in the water chemically equivalent amounts of acids and bases. The water would then be described as being neutral; i.e., there is a preponderance of neither acid nor basic materials. The occurrence of such a condition would be rare.

2 The term "neutralization" refers to the combining of chemically equivalent amounts of acids and bases. The two products of neutralization are a salt and water.

HCl	+	$NaOH$	=	$NaCl + H_2O$
Hydrochloric acid		Sodium Hydroxide		Sodium Chloride (a salt)

D Acidity and/or alkalinity are measurements of a gross property of a water rather than of specific acids or bases present.

III HOW ARE DEGREES OF ACIDITY AND ALKALINITY EXPRESSED?

The pH scale is used to express various degrees of acidity and alkalinity. Values can range from 0 to 14. These two extremes are of theoretical interest and are not often encountered in a natural water or in a waste water. pH readings from 0 to just under 7 indicate an acidic condition; from just over 7 to 14, an alkaline condition. Neutrality exists if the pH value is exactly 7. pH paper or a pH meter provides the most convenient method of obtaining pH readings. It should be noted, that under NPDES* Methodology, pH measurements are to be made using a pH meter. Some common liquids and pH values are listed in Table I.

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*National Pollutant Discharge Elimination System.

TABLE 1. pH Values of Common Liquids

Household lye	13.7
Bleach	12.7
Ammonia	11.3
Milk of magnesia	10.2
Borax	9.2
Baking soda	8.3
Sea water	8.0
Blood	7.3
Distilled water	7.0
Milk	6.8
Corn	6.2
Boric acid	5.0
Orange juice	4.2
Vinegar	2.8
Lemon juice	2.2
Battery acid	0.2

5.9 - 8.4 is the common pH range for most natural waters.

IV HARD AND SOFT WATERS

In addition to being acidic or basic, water can also be described as being hard or soft.

A Hard water contains large amounts of calcium, magnesium, strontium, manganese and iron ions, relative to the amount of sodium and potassium ions present. Hard water is objectionable because it forms insoluble compounds with ordinary soap.

B Soft water contains small amounts of calcium, magnesium, strontium, manganese and iron ions, relative to the amount of sodium and potassium ions present. Soft water does not form insoluble compounds with ordinary soap.

V TITRATIONS

A The conversion of pH readings into such quantities as milligrams (mg) of acidity, alkalinity, or hardness, is not easily carried out. These values are more easily obtained by means of a titration.

B In a titration, an accurately measured volume of sample (of unknown strength) is combined with an accurately measured volume of standard solution (of known strength) in the presence of a suitable indicator.

C The strength (called normality) of the sample is then found using the following expression:

milliliters (ml) of sample × normality (N) of sample = ml of standard solution × N of standard solution.

Three of the four quantities are known, and

N of sample = ml of standard solution × N of standard solution/ml of sample.

D In modified form, and a more specific application of the above equation, alkalinity is calculated in the following manner:

mg of alkalinity as mg $CaCO_3$/liter (l) = ml of standard H_2SO_4 × N of standard H_2SO_4 × 50 × 1000/ml sample.

VI INDICATORS

The term "suitable indicator" was used above. At the end of a titration, the pH of the solution will not necessarily be 7. It may be above or below 7. A suitable indicator, therefore, is one which undergoes its characteristic color change at the appropriate pH. Below are a few examples of indicators and the pH range in which they undergo their characteristic color changes. In some cases, mixed indicators may be used in order to obtain a sharper and more definite color change. Again it should be noted that under NPDES, pH meters are to be used for the measurement of pH.

Indicator	Operational pH Range
Methyl Yellow	2.8 - 4.0
Methyl Orange	3.1 - 4.4
Methyl Red	4.4 - 6.2
Cresol Purple	7.4 - 9.0
Phenolphthalein	8.0 - 9.6
Alizarine Yellow	10.0 - 12.0

TABLE 2. pH Range of Indicators

VII BUFFERS

A A buffer is a combination of substances which, when dissolved in water, resists a pH change in the water, as might be caused by the addition of acid or alkali. Listed below are a few chemicals which, when combined in the proper proportions, will tend to maintain the pH in the indicated range.

Chemicals	pH Range
Acetic Acid + Sodium Acetate	3.7 - 5.6
Sodium Dihydrogen Phosphate + Disodium Hydrogen Phosphate	5.8 - 8.0
Boric Acid + Borax	6.8 - 9.2
Borax + Sodium Hydroxide	9.2 - 11.0

TABLE 3. pH Range of Buffers

B A buffer functions by supplying ions which will react with hydrogen ions (acid "spill"), or with hydroxide ions (alkali "spill").

C In many instances, the buffer is composed of a weak acid and a salt of the weak acid; e.g., acetic acid and sodium acetate.

1 In water, acetic acid ionizes or "breaks down" into hydrogen ions and acetate ions.

$$\underset{\text{(acetic acid)}}{HC_2H_3O_2} = \underset{\substack{\text{(hydrogen ion)}\\\text{(proton)}}}{H^+} + \underset{\text{(acetate ion)}}{C_2H_3O_2^-}$$

This ionization occurs to only a slight extent, however, most of the acetic acid remains in the form of $HC_2H_3O_2$; only a small amount of hydrogen and acetate ions is formed.

2 Thus, acetic acid is said to be a weak acid.

3 In the case of other acids, ionization into the component ions occurs to a large degree, and the term strong acid is applied; e.g., hydrochloric acid.

$$\underset{\substack{\text{(hydrochloric}\\\text{acid)}}}{HCl} = \underset{\substack{\text{(hydrogen ion)}\\\text{(proton)}}}{H^+} + \underset{\substack{\text{(chloride}\\\text{ion)}}}{Cl^-}$$

4 The terms "strong" and "weak" are also applied to bases. In water solutions, those which break down into their component ions to a large extent are termed "strong", and those which do not are "weak". Sodium hydroxide is a relatively strong base, while ammonium hydroxide is realtively weak.

5 Sodium acetate (a salt of acetic acid) dissociates or "breaks down" into sodium ions and acetate ions when placed in water.

$$\underset{\text{(sodium acetate)}}{NaC_2H_3O_2} = \underset{\text{(sodium ion)}}{Na^+} + \underset{\text{(acetate ion)}}{C_2H_3O_2^-}$$

This dissociation occurs to a large extent, and practically all of the sodium acetate is in the form of sodium ions and acetate ions.

D It would be difficult and expensive to prepare large quantities of buffers for use in a treatment plant. However, certain naturally occurring buffers may be available (carbon dioxide is an example). It dissolves in water to form the species indicated below.

$$\underset{\text{(carbon dioxide)}}{CO_2} + \underset{\text{(Water)}}{H_2O} = \underset{\text{(carbonic acid)}}{H_2CO_3}$$

$$H_2CO_3 = \underset{\substack{\text{(hydrogen ion)}\\\text{(proton)}}}{H^+} + \underset{\substack{\text{(hydrogen carbonate ion)}\\\text{(bicarbonate)}}}{HCO_3^-}$$

The hydrogen ions react with hydroxide ions which might appear in the water as the result of an alkali "spill".

$$\underset{\substack{\text{(in the}\\\text{buffer)}}}{H^+} + \underset{\substack{\text{(hydroxide ion}\\\text{"spilled")}}}{OH^-} = H_2O$$

The hydrogen carbonate ions react with hydrogen ions which might appear in the water as the result of an acid "spill".

$$\underset{\substack{\text{(hydrogen ion)}\\\text{(proton)}\\\text{"spilled"}}}{H^+} + \underset{\substack{\text{(in the}\\\text{buffer)}}}{HCO_3^-} = H_2CO_3$$

This buffering action will be in effect as long as there is carbonic acid present.

E Buffering action is not identical with a process in which acid wastes are "neutralized" with alkali wastes, or conversely. The desired effect is achieved in both cases, however (i.e. the pH is maintained within a desired range.)

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Descriptors: Acids, Acidity, Alkalis, Alkalinity, Analytical Techniques, Buffers, Buffering Capacity, Chemical Analysis, Hydrogen Ion Concentration, Indicators, Neutralization, Water Analysis.

ALKALINITY AND RELATIONSHIPS AMONG THE VARIOUS TYPES OF ALKALINITIES

I PRELIMINARY

The property of water referred to as alkalinity is usually caused by the presence of hydroxyl, carbonate and bicarbonate ions. To a lesser extent, borates, phosphates and silicates contribute but are generally present in negligible amounts.

The concentration and ratio of the OH^-, CO_3^{--}, and HCO_3^- ions may be measured by titrating a sample to certain specified pH's or end points which are detected either by use of a pH meter or by color indicators. Phenolphthalein is used for visual detection of the first end point, (approximately pH 8) which indicates the neutralization of NaOH and conversion of CO_3^{--} to HCO_3^-. A number of indicators (methyl orange, methyl purple, brom cresol green,etc.) are used for detection of the second end point (pH 3-5) which indicates the complete conversion of HCO_3^- to H_2O and CO_2. The final end point is determined by the amount of CO_3^{--} and HCO_3^- originally present in the sample. If the end points are determined electrometrically they are taken as the mid-point of the greatest rate of pH change per unit volume of titrant.

II RELATIONSHIPS BETWEEN HYDROXIDE, CARBONATE, AND BICARBONATE ALKALINITIES

The results obtained from phenolphthalein and total alkalinity measurements offer a means of classification of the principal forms of alkalinity, if certain assumptions are made. It must first be assumed that interferences are absent and that bicarbonate and hydroxide do not exist in the same solution. According to the system presented in Standard Methods (1):

A Hydroxide alkalinity is present if the phenolphthalein alkalinity is more than one-half the total alkalinity.

B Carbonate alkalinity is present if the phenolphthalein alkalinity is not zero but is less than the total alkalinity.

C Bicarbonate alkalinity is present if the phenolphthalein alkalinity is less than one-half the total alkalinity.

Table 1. Relationships Between Phenolphthalein Alkalinity, Total Alkalinity, Carbonate Alkalinity, Bicarbonate Alkalinity and Hydroxide Alkalinity

Lecture Notes	Result of Titration	OH^- Alkalinity as $CaCO_3$	CO_3^{--} Alkalinity as $CaCO_3$	HCO_3^- Alkalinity as $CaCO_3$
Case 1	$P = T$	T	O	O
Case 2	$P = \frac{1}{2}T$	O	2P	O
Case 3	$P = O$	O	O	T
Case 4	$P > \frac{1}{2}T$	2P-T	2(T-P)	O
Case 5	$P < \frac{1}{2}T$	O	2P	T-2P

P = Phenolphthalein Alkalinity T = Total Alkalinity

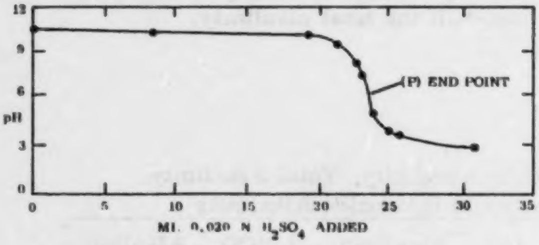
Table 2. Stoichiometric Volumes of Solutions of Different Normalities

Standard Solution	H_2SO_4	NaOH	Na_2CO_3	$NaHCO_3$
Normality	0.0200	0.0189	0.0199	0.0125
Equivalent Volumes, ml	10.0	10.6	9.9	16.0
	9.4	10.0	9.5	15.1
	10.0	10.5	10.0	15.9
	6.3	6.6	6.3	10.0

III CASE EXAMPLES

The relationships involved in Table 1 may best be explained by reference to the following graphs. These were prepared by titrating volumes of standard solutions of sodium hydroxide, sodium carbonate, and sodium bicarbonate with standard sulfuric acid. The stoichiometric volumes of the various solutions are summarized in Table 2 for convenience in the interpretation of the charts.

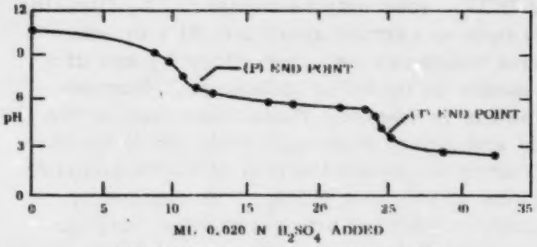
A CASE 1 - Where phenolphthalein alkalinity = total alkalinity



25 ML 0.0180 N NaOH vs 0.020 N H_2SO_4
(P = T)

The sharp break occurs at the point where all of the NaOH has been exactly neutralized by the acid. The pH and concentration of the end products (Na_2SO_4 and H_2O) determine the pH at the equivalence point between NaOH and H_2SO_4; in this case, approximately 7.0.

B CASE 2 - Where phenolphthalein alkalinity = one-half the total alkalinity

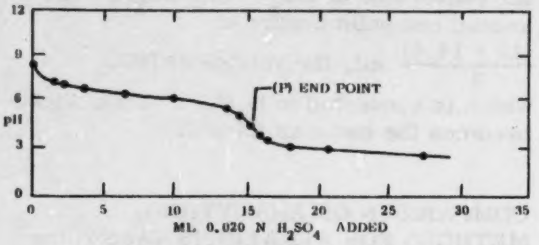


25 ML 0.020 N Na_2CO_3 vs 0.020 N H_2SO_4
(P = ½ T)

The titration proceeds in 2 stages wherein all of the CO_3^{--} is converted, first to HCO_3^- and finally to H_2CO_3. The first end point occurs at approximately pH 8, and at exactly half the volume of acid used for the total titration. The end point which occurs at approximately pH 4 represents the total alkalinity and requires exactly twice the volume of acid used for the first end point.

If either HCO_3^- or OH^- ions had been present the titration volumes for the curves would not have been of equal magnitude.

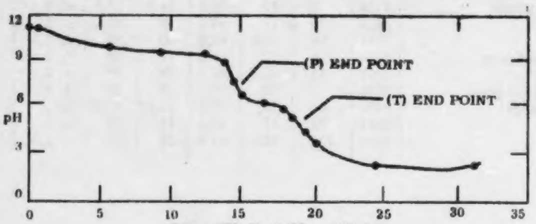
C CASE 3 - Where phenolphthalein alkalinity = 0



25 ML 0.0125 N $NaHCO_3$ vs 0.020 N H_2SO_4
(P = O)

T The reaction proceeds in one stage with the initial pH at approximately 8.5 and final pH at 4.0. In this case the phenolphthalein alkalinity is zero and since no conversion of CO_3^{--} to HCO_3^- is noted the total alkalinity can only be due to the HCO_3^- ion.

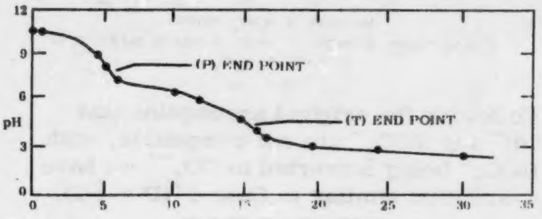
D CASE 4 - Where phenolphthalein alkalinity is greater than one-half the total alkalinity



[10 ML 0.0180 N NaOH + 10 ML 0.020 N Na_2CO_3] vs 0.020 N H_2SO_4
(P > ½ T)

The volume of acid required for the first end point (phenolphthalein alkalinity) is due to the OH^- neutralization and conversion of the CO_3^{--} to HCO_3^-. The second end point represents the complete conversion of HCO_3^- to H_2CO_3. Referring to Case 2 where the volume of acid was similar for each end point, it is apparent that a base responding to phenolphthalein but which is not CO_3^{--} must be present. Since it was originally assumed that OH^- and HCO_3^- do not exist in the same solution we must conclude that the total alkalinity is due to OH^- and CO_3^{--}.

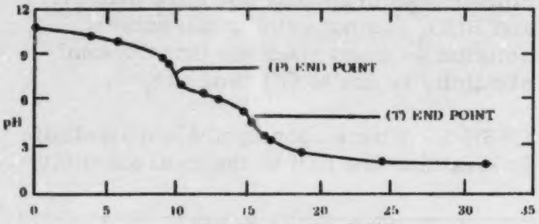
E CASE 5 - Where phenolphthalein alkalinity is less than one half of the total alkalinity



[10 ML 0.020 N Na_2CO_3 + 10 ML 0.125 N $NaHCO_3$] vs 0.020 N H_2SO_4
(P < ½ T)

If, in the reaction $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$, the NaOH exists in excess quantity, the final sample contains NaOH and Na_2CO_3, (Case 4) in which the volume of acid required for the phenolphthalein end point is greater than one half the total. In this case, however, the situation is reversed, wherein the volume of acid required for the HCO_3^- end point is greater than one half the total. Referring again to the reaction $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$, if $NaHCO_3$ is in excess the end products must consist of Na_2CO_3 and $NaHCO_3$ and OH^- must be absent. The end points consist, therefore, of $Na_2CO_3 \rightarrow NaHCO_3$ (phenolphthalein end point) and $NaHCO_3 \rightarrow H_2CO_3$.

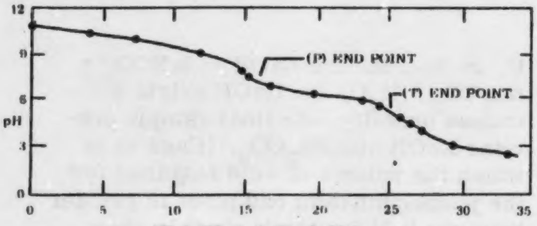
F CASE 6 - Where phenolphthalein alkalinity is greater than one-half total alkalinity.



[10 ML 0.0180 N NaOH + 10 ML 0.0125 N $NaHCO_3$] vs 0.020 N H_2SO_4
(P > T)

Following the original assumption that OH^- and HCO_3^- are not compatible, with HCO_3^- being converted to CO_3^{--} we have a condition similar to Case 4 $(P > \frac{1}{2}T)$.

G CASE 7 - Where phenolphthalein alkalinity is greater than one-half total alkalinity.



[10ML 0.0180 N NaOH + 10 ML 0.020 N Na_2CO_3 + 10 ML 0.0125 N $NaHCO_3$] vs 0.020 N H_2SO_4
(P > T)

The first end point occurs at the stoichiometric sum of the equivalent volumes as follows:

$$(9.4 - 6.3) + \frac{(10 + 12.6)}{2}$$

where $(9.4 - 6.3)$ = volume of N acid required for excess OH^- after OH^- + HCO_3^- reaction, and $\frac{(10 + 12.6)}{2}$ = volume of acid required for conversion of CO_3^{--} to HCO_3^-. The second end point occurs at $\frac{(10 + 12.6)}{2}$ ml, the volume of HCO_3^- which is converted to H_2CO_3. This, then, becomes the same as Case 4.

IV COMPARISON OF ANALYTICAL METHODS FOR ALKALINITY (According to the Analytical Reference Service Report JAWWA Vol. 55, No. 5, 1963)

May 1963 DETERMINATION METHODS

TABLE 2—*Statistical Summary (contd.)*

Method	Year	No. of Values Reported	Concn. Added mg/l	Concn. Determined mg/l			50% Range mg/l	Standard Deviation mg/l
				Mean	Low	High		
Alkalinity								
Methyl orange	1956	38	19	20.0	11.23	30.0	± 2	5.049
	1958	19	17	19.5	16	24	± 1	2.483
	1961	27	42.5	43.7	38	50	± 1.5	3.250
Electrometric	1956	14	19	19.7	19.0	21.0	± 1	0.911
	1958	53	17	19.4	15	25	± 2	2.740
	1961	88	42.5	44.2	38.9	57	± 2.5	3.605
Methyl purple	1956	8	19	14.7	14.0	15.2	± 4	0.475
	1958	10	17	19.3	18	21	± 2	0.823
	1961	18	42.5	44.8	40	50	± 1.5	3.081
Mixed indicator	1958	4	17	19.5	18	20	± 3	1.000
	1961	15	42.5	42.8	39	49	± 3	3.550
Brom cresol green	1958	1	17	19	19	19	± 2	
All methods	1956	60	19	19.2	11.23	30.0	± 2	4.460
	1958	92	17	19.6	15	25	± 2	2.320
	1961	178	42.5	43.9	25	57	± 1.9	5.335

Alkalinity - The methods for alkalinity measurement varied only in the choice of indicator or pH for determining the end point of the titration. The indicators used included methyl orange, methyl purple, and mixed indicator. The data shows that as the use of electrometric end point increased, the use of methyl orange decreased.

SUMMARY

Amount Added	17 mg/l (as $CaCO_3$)
Avg. Deviation from amount added	3.1 mg/l
Standard Deviation	3.4 mg/l
50% Range	2.0 mg/l
Method Most Commonly Used	Electrometric
Method Preferred	Electrometric
Total Number of Observations	41

V PROCEDURE

The actual measurement of alkalinity is a very simple procedure requiring only titration of sample with a standardized acid and the proper indicator. For phenolphthalein alkalinity, the end point and indicator are well established. For the bicarbonate titration the final end point is a function of the HCO_3^- concentration. With low amounts (< 50 mg/l as $CaCO_3$) the pH at end point may be approximately 5.0. With high concentrations (> 250 mg/l as $CaCO_3$) the pH at end point may be 4.5 to 3.8. For all-purpose work, in which the highest degree of accuracy is not required, an end point at pH 4.5 using methyl purple as the indicator is recommended.

The traditional methyl orange frequently proves to be unsatisfactory because of the indefinite color change at the end point and also because of the low pH (3.8 - 3.9) required to establish the change.

VI EPA ANALYTICAL METHODS

A The Environmental Protection Agency, Office of Water Programs, has compiled a manual of Analytical Methods which is to be used in Federal laboratories for the chemical analysis of water and waste samples. The title of this manual is "Methods for Chemical Analysis of Water and Wastes."(2)

B This manual lists two parameters which are related to the subject matter in this outline. They are total alkalinity and total acidity.

C For the measurement of both of these parameters, the recommended method is volumetric, with the equivalence point being determined electrometrically. The use of a color indicator (methyl orange) is recommended only for the automated method.

REFERENCES

1 Standards Methods for the Examination of Water and Wastewater, 14th Ed. APHA, Inc., New York. 1976

2 Methods for Chemical Analysis of Water and Wastes, EPA-MDQARL, Cincinnati, Ohio 45268, 1974.

This outline was prepared by R. C. Kroner, former Chief, Physical and Chemical Methods, Analytical Quality Control Laboratory, National Environmental Research Center, Cincinnati, Ohio 45268.

Descriptors: Alkalis, Alkalinity, Analytical Techniques, Buffers, Buffering Capacity, Chemical Analysis, Water Analysis

DETERMINATION OF CALCIUM AND MAGNESIUM HARDNESS

I INTRODUCTION

A Definition of Hardness

USPHS - "In natural waters, hardness is a characteristic of water which represents the total concentration of just the calcium and magnesium ions expressed as calcium carbonate. If present in significant amounts, other hardness-producing metallic ions should be included."

B Other Definitions in Use

1 **Some confusion exists in understanding the concept of hardness as a result of several definitions presently used.**

2 **Soap hardness definition includes hydrogen ion because it has the capacity to precipitate soap. Present definition excludes hydrogen ion because it is not considered metallic.**

3 **Other agencies define hardness as "the property attributable to presence of alkaline-earths".**

4 **USPHS definition is best in relation to objections of hardness in water.**

II CAUSES OF HARDNESS IN WATERS OF VARIOUS REGIONS OF THE U. S.

A Hardness will vary throughout the country depending on:

1 **Leaching action of water traversing over and through various types of geological formations.**

2 **Discharge of industrial and domestic wastes to water courses.**

3 **Uses of water which result in change in hardness, such as irrigation and water softening process.**

B Objections to Hardness

1 **Soap-destroying properties**

2 **Scale formation**

C Removal and Control

Hardness may be removed and controlled through the use of various softening operations such as zeolite, lime-soda, and hot phosphate processes. It can also be removed by simple distillation or complex formation with surface active agents (detergents).

III ANALYTICAL PROCEDURES

A National Pollutant Discharge Elimination System (NPDES)

Under the NPDES of the 1972 Federal Water Pollution Control Act Amendments, analyses are to be performed using "approved" analytical procedures cited in the Federal Register Guidelines Establishing Test Procedures for the Analysis of Pollutants. The cited procedures are found in Standard Methods(1), Annual Book of ASTM Standards(2), and Methods for Chemical Analysis of Water and Wastes(3). The three relevant parameters are: total hardness, total and dissolved calcium, and total and dissolved magnesium.

B Total Hardness

1 **Total hardness may be determined by titrating the buffered sample with ethylenediamine tetraacetic acid (EDTA) at a pH of 10.0 ± 0.1 using a dye such as Eriochrome Black T indicator. A color change from rose to blue is the end-point. Either daylight or a fluorescent lamp should be used for illumination. Incandescent lights produce a reddish tinge at the end-point. Certain metals such as iron, manganese, nickel, zinc and others, interfere with end-point clarity.**

Chemical inhibitors are needed to tie up the interferring metals. Some inhibitors contain sodium cyanide, and extreme caution must be observed when they are used.

2 In the automated procedure, magnesium EDTA exchanges magnesium for calcium. The released magnesium, plus the magnesium already present in the sample, produces a red violet complex with calmagite at a pH of 10. The total hardness (i. e., calcium plus magnesium) is determined therefore, by analysis for magnesium.

C Digestion(7)

When determining Total Calcium or Total Magnesium, the initial step is digestion. The sample is first acidified with concentrated redistilled HNO_3(5 ml/l). Five ml of distilled HCl(50% by volume) are next added to 100 ml of the well-mixed acidified sample, which is then heated at 95°C for 15 minutes. The sample is next diluted back to 100 ml for analysis.

D Total Calcium

1 Total calcium may also be determined by titration with EDTA, at a pH of 12-13. Murexide, Eriochrome Blue Black R, and Solochrome Dark Blue are among the indicators which may be used. The titration should be carried out immediately after raising the pH. Lower concentrations (e.g., less than 20 mg/l) of certain metals such as copper, ferric and ferrous iron, manganese and zinc do not interfere. However orthophosphate precipitates calcium at the elevated pH of the test. Strontium and barium interfere, and alkalinity greater than 30 mg/l causes an indistinct end-point.

2 Lanthanum is used to mask the phosphate, sulfate and aluminum interference in the atomic absorption determination of calcium. High concentrations (up to 500 mg/l) of sodium, potassium, and nitrate cause no difficulty. Magnesium levels greater than 1000 mg/l cause low results.

E Total Magnesium

1 The gravimetric determination of magnesium involves addition of diammonium hydrogen phosphate which precipitates magnesium ammonium phosphate. The precipitate is ignited and weighed as magnesium pyrophosphate. The sample should be reasonably free of aluminum, calcium, iron, manganese, silica, strontium, and suspended matter.

2 Aluminum concentrations greater than 2 mg/l interfere with the atomic absorption procedure. Lanthanum is used as a masking agent. At concentrations less than 400 mg/l, sodium, potassium and calcium cause no problem..

F Dissolved Calcium & Dissolved Magnesium

The dissolved metals are determined by 0.45 μm filtration, followed by acidification with redistilled HNO_3 to a pH of 2, and the method (except for digestion) used for the "Total" metal. Pre-filtration to remove larger suspended solids is permissable. A glass or plastic filtration apparatus is recommended to avoid contamination.

G Other Procedures

1 The analytical procedures for total hardness, calcium and magnesium outlined above are those to be performed under the NPDES.

2 Examples of other, "non-NPDES" procedures are:

a Gravimetric determination of calcium.

b Potassium permanganate titration of calcium.

c Determination of total hardness and calcium or magnesium and then subtracting to obtain the concentration of the other metal. This procedure assumes that calcium and magnesium are the only hardness components present.

d Determining the concentration of the individual metals, multiplying the concentrations by an appropriate factor to put the values on a calcium carbonate basis, and then summing the calcium carbonate concentrations to obtain a total hardness value.

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater, 14th ed. APHA, AWWA, WPCF, 1975.

2 Annual Book of ASTM Standards, Part 31, 1975.

3 Methods for Chemical Analysis of Water and Wastes, EPA-EMSL Cincinnati, Ohio 45268, 1974.

4 Barnard, A. J. Jr., Broad, W. C. and Flaschka, H. The EDTA Titration. J. T. Baker Company. 1957.

5 U. S. Public Health Service. Drinking Water Standards. USPHS Report, Volume 61, No. 11, 1946.

6 Rainwater, R. H. and Thatcher, L. L. Methods for the Collection and Analysis of Water Samples. U. S. Geological Survey Water Supply, Paper 1454. 1960.

7 Federal Register, Wednesday, Dec. 1, 1976, Part II, Table 1, footnote 15.

This outline was prepared by B. V. Salotto, Research Chemist, Waste Identification and Analysis Section, MERL, EPA, and revised by C. R. Feldmann, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Calcium, Chemical Analysis, Hardness, Magnesium, Water Analysis, Calcium Carbonate, Calcium Compounds, Magnesium Carbonate

CHLORINATION AND CHLORINE DETERMINATIONS

I INTRODUCTION

Chlorine normally is applied to water as a bactericidal agent; it reacts with water contaminants to form a variety of products containing chlorine. The difference between applied and residual chlorine represents the chlorine demand of the water under conditions specified. Wastewater chlorination is particularly difficult because the concentration of organisms and components susceptible to interaction with chlorine are high and variable. Interferences with the chlorine determination in wastewater confuse interpretation with respect to the chlorine residual at a given time and condition, its bactericidal potency, or its future behavior.

II CHEMISTRY OF CHLORINATION

Chlorine is used in the form of chlorine gas, chlorine gas dissolved in water or as hypochlorites.

A Chlorine (Cl_2) combines with water to form hypochlorous and hydrochloric acids:

$$Cl_2 + H_2O \rightleftarrows HOCl + H^+ + Cl^-$$

The reaction is reversible, but at pH values above 4.0 and concentrations of chlorine below 1000 mg/L the shift is predominantly to the right leading to hypochlorous acid (HOCl). Hypochlorous acid is a weak acid and consequently ionizes in water according to the equation:

$$HOCl \rightleftarrows H^+ + OCl^-$$

This reaction is also reversible. At a pH value of 6.0 or below almost all of the chlorine is present as hypochlorous acid (HOCl) whereas above pH 10.0 nearly all of it exists as hypochlorite ion (OCl). Thus the addition of chlorine (Cl_2) tends to lower the pH.

B One hypochlorite compound used for water treatment is calcium hypochlorite. When dissolved in water it forms hypochlorous acid and calcium hydroxide:

$$Ca(OCl)_2 + 2H_2O \rightleftarrows 2HOCl + Ca^{++} + 2OH^-$$

The hypochlorous acid ionizes as shown below:

$$HOCl \rightleftarrows H^+ + OCl^-$$

Thus treatment with a hypochlorite results in the same equilibrium as when chlorine is added. A contrast, though, is the increase in pH when metallic hypochlorites are applied because of the formation of OH^-.

C The initial reactions on adding chlorine to wastewaters may be assumed to be fundamentally the same as when chlorine is added to water except for the additional complications due to contaminants and their concentration.

Hypochlorous acid (HOCl) reacts with ammonia and with many other complex derivatives of ammonia to produce compounds known as chloramines. Formation of the simple ammonia chloramines includes:

1 $NH_3 + HOCl \rightarrow NH_2Cl + H_2O$

monochloramine

2 $NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$

dichloramine

3 $NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$

trichloramine

The distribution of the ammonia chloramines is dependent on pH, as illustrated below:

	Percentage of Chlorine Present as	
pH	Monochloramine	Dichloramine
5	16	84
6	38	62
7	65	35
8	85	15
9	94	6

The mono- and dichloramines have significant disinfecting power. Their formation is dependant on pH, temperature, and chlorine-ammonia ratio. Chlorine reactions with amino acids are also likely, but the product disinfecting powers are lower than those of the hypochlorite ion or of ammonia chloramines.

III TERMINOLOGY

A Terms used with Respect to Application Site

1 Pre-chlorination - chlorine added prior to any other treatment.

2 Post-chlorination - chlorine added after other treatment.

3 Split chlorination - chlorine added at different points in the plant - may include pre- and post-chlorination.

B Terms Used in Designating Chlorine Fractions

1 Free available residual chlorine - the residual chlorine present as hypochlorous acid and hypochlorite ion.

2 Combined available residual chlorine - the residual chlorine present as chloramines and organic chlorine containing compounds.

3 Total available residual chlorine - the free available residual chlorine + the combined available residual chlorine - may represent total amount of chlorine residual present without regard to type.

In ordinary usage these terms are shortened to free residual chlorine, combined residual chlorine and total residual chlorine. In the chlorination of wastewaters only combined residual chlorine is ordinarily present and is often improperly termed chlorine residual.

C Breakpoint chlorination specifically refers to the ammonia-chlorine reaction where applied chlorine hydrolyzes and reacts to form chloramines and HCl, with the chloramines eventually forming N_2 and HCl:

$$NH_2Cl + NHCl_2 \longrightarrow N_2 + 3HCl$$

Assuming no other chlorine demand, the total chlorine residual will rise, decrease to zero and rise again with increasing increments of applied chlorine. Other substances may produce humps in the applied chlorine vs residual chlorine plot due to oxidation of materials other than ammonia. Sometimes these are erroneously considered as a breakpoint.

IV IODOMETRIC TITRATION ANALYSES(1, 2)

Iodometric titration using either an amperometric or a starch-iodine end point determines chlorine residual. The relative advantages of a specific determination depend upon the form in which the reactable chlorine exists and the amount and nature of interferences in the water.

A Amperometric Titration - Direct Method

1 Scope and application

This method is applicable to the determination of free, combined or total residual chlorine in all types of water and wastewaters that do not contain substantial amounts of organic matter.

2 Summary of Method

When the cell of the titrator is immersed in a sample at pH 7.0, the cell unit produces a small direct current if free chlorine (an oxidizing agent) is present. As phenylarsine oxide (PAO) solution is added, it reduces the free chlorine. When all the chlorine is neutralized, the generation of current ceases. At this end point, the microammeter pointer on the apparatus no longer deflects down-scale.

To determine combined chlorine, pH 4.0 buffer and potassium iodide are then added to the sample. Free iodine released by the combined chlorine also causes the cell to produce a small direct current. Addition of PAO reduces the free iodine and the generation of current ceases. Again, the end point occurs when the microammeter pointer no longer deflects down-scale.

In either titration, the amount of PAO reducing agent used to reach the end point is ultimately stoichiometrically proportional to chlorine present in the sample. The sum of the free and combined chlorine is the total residual chlorine in the sample.

Total residual chlorine can be determined directly by adding pH 4.0 buffer and potassium iodide to the sample before beginning the titration. Any free or combined chlorine present will stoichiometrically liberate free iodine which is then reduced with PAO titrant. The amount of PAO titrant used measures the total amount of free and combined chlorine originally present in the sample.

3 Interferences

a Organic matter reacts with liberated iodine.

b Cupric ions may cause erratic behavior of the apparatus.

c Cuprous and silver ions tend to poison the electrode by plating out on it.

B Amperometric Titration - Indirect Method

1 Scope and Application

This method is applicable to the determination of total chlorine residual in all types of water and wastewaters. In contrast to the direct amperometric titration, this back-titration procedure minimizes interferences in waters containing substantial amounts of organic matter.

2 Summary of Method

A sample is treated with a measured excess of standard phenylarsine oxide (PAO) solution followed by addition of potassium iodide and a buffer to maintain the pH between 3.5 and 4.2.

Any form of chlorine present will stoichiometrically liberate iodine which immediately reacts with the PAO before significant amounts are lost to reactions with organic matter in the sample.

When the cell of the amperometric titrator is immersed in a sample so treated, no current is generated since neither free chlorine nor free iodine is present.

The amount of PAO used to reduce the liberated iodine is then determined by titrating the excess with a standard iodine solution. No current is generated until all the excess PAO has been oxidized by the iodine. At this end point the next small addition of iodine causes current to be generated and the microammeter pointer permanently deflects up-scale.

The excess PAO thus measured is subtracted from the original amount of PAO added. The difference is the PAO used to reduce the liberated iodine and is ultimately a measure of the total chlorine originally present in the sample.

NOTE: Sodium thiosulfate solution may be used instead of PAO, but PAO is more stable and is to be preferred.

3 Interferences

a Cupric ions may cause erratic behavior of the apparatus.

b Cuprous and silver ions tend to poison the electrode by plating out on it.

C Colorimetric Starch-Iodide Titration - Indirect Method

1 Scope and Application

This method is applicable to the determination of total chlorine residual in all types of water and wastewater. A back-titration procedure is used to minimize interferences in waters containing substantial amounts of organic matter.

2 Summary of Method

A sample is treated with a measured excess of standard phenylarsine oxide (PAO) solution followed by addition of potassium iodide and a buffer to maintain the pH between 3.5 and 4.2. Any form of chlorine present will stoichiometrically liberate iodine which immediately reacts with PAO before significant amounts are lost to reactions with organic matter in the sample.

The amount of PAO used to reduce the liberated iodine is then determined by titrating the excess with a standard iodine solution in the presence of starch until the PAO is completely oxidized. At this end point, the next small addition of iodine causes a faint blue color to persist in the sample.

The excess PAO thus measured is subtracted from the original amount of PAO added. The difference is the PAO used to reduce the liberated iodine and is ultimately a measure of the total chlorine originally present in the sample.

NOTE: Sodium thiosulfate solution may be used instead of PAO, but PAO is more stable and is to be preferred.

3 Interferences

a An unusually high content of organic matter may cause some uncertainty in the end point. If manganese, iron and nitrite are definitely absent, this uncertainty can be reduced by acidification to pH 1.0.

b Color and turbidity in the sample cause difficulty with end-point detection.

D Evaluation of Iodometric Analyses

Iodometric titration using amperometric end point detection appears to be the more accurate residual chlorine method Besides being inherently more accurate than color detection methods, this electrical end point is free of interference from color and turbidity.

The accuracy of the colorimetric starch-iodide end point is improved by employing the indirect titration method described above. By adding an excess of the standard reducing agent and back-titrating, contact between the liberated iodine and organic matter in the sample is minimized.

V DPD METHODOLOGY(1)

The DPD (N-diethyl-phenylenediamine) method can be applied by either titration or spectrophotometry.

A Titration

1 Scope and Application

This method is applicable to natural and treated waters at concentrations above 1 mg/liter chlorine.

2 Summary of Method

A sample is treated with a buffer to maintain pH 4 or less, followed by addition of DPD indicator and potassium iodide. Chlorine (hypochlorite ion, hypochlorous acid) and chloramines present in the sample will stoichiometrically liberate iodine from the potassium iodide.

The liberated iodine is titrated with ferrous ammonium sulfate to the disappearance of the red color with the DPD serving as the indicator. Results represent total available residual chlorine. The titration can be conducted in stages to distinguish among free available chlorine, monochloramine and dichloramine. Nitrogen trichloride can also be estimated by changing the order of the steps of procedure.

B Spectrophotometry

1 Scope and Application

This method is applicable to natural and treated waters at concentrations from 0.2 to 4 mg/liter.

2 Summary of Method

The sample is treated in the same manner as in the titration procedure, only smaller quantities of reagents and sample are used. The reactions liberating iodine are the same.

Quantitation requires spectrophotometric readings at 515 nm of the absorbance of the red colors produced in the treated samples. The concentrations are determined using a calibration graph developed from a series of potassium permanganate standards covering the chlorine equivalent range of 0.05 - 4 mg/liter.

VI COMPLIANCE METHODOLOGY

A NPDES/Certifications

All of the analytical procedures described in IV, Iodometric Titration Analyses and in V, DPD Methodology (above) are cited in the Federal Register as approved.

B Drinking Water

Under certain conditions, chlorine residual monitoring can be substituted for some of the microbiological tests required by drinking water regulations. Only the DPD Methodology (as in V above) is cited in the Federal Register as approved for this application. In contrast to the NPDES/Certifications regulations, the DPD test kit is also approved for drinking water samples.

ACKNOWLEDGEMENT:

Significant portions of this outline were written by J. L. Holdaway, Chemist Technical Program, USEPA, Region III, Charlottesville, VA 22901 (1971) and by Charles R. Feldmann, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

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Descriptors: Chemical Analysis, Chlorination, Chlorine, Disinfection, Sewage Treatment, Wastewater Treatment, Water Analysis.

PHOSPHORUS IN THE AQUEOUS ENVIRONMENT

I Phosphorus is closely associated with water quality because of (a) its role in aquatic productivity such as algal blooms, (b) its sequestering action, which causes interference in coagulation, (c) the difficulty of removing phosphorus from water to some desirable low concentration, and (d) its characteristic of converting from one to another of many possible forms.

A Phosphorus is one of the primary nutrients such as hydrogen (H), carbon (C), nitrogen (N), sulfur (S) and phosphorus (P).

1 Phosphorus is unique among nutrients in that its oxidation does not contribute significant energy because it commonly exists in oxidized form.

2 Phosphorus is intimately involved in oxidative energy release from and synthesis of other nutrients into cell mass via:

a Transport of nutrients across membranes into cell protoplasm is likely to include phosphorylation.

b The release of energy for metabolic purposes is likely to include a triphosphate exchange mechanism.

B Most natural waters contain relatively low levels of P (0.01 to 0.05 mg/L) in the soluble state during periods of significant productivity.

1 Metabolic activity tends to convert soluble P into cell mass (organic P) as a part of the protoplasm, intermediate products, or sorbed material.

2 Degradation of cell mass and incidental P compounds results in a feedback of lysed P to the water at rates governed by the type of P and the environment. Aquatic metabolic kinetics show marked influences of this feedback.

3 The concentrations of P in hydrosoils, sludges, treatment plant samples and soils may range from 10^2 to 10^6 times that in stabilized surface water. Both concentration and interfering components affect applicability of analytical techniques.

II The primary source of phosphorus in the aqueous system is of geological origin. Indirect sources are the processed mineral products for use in agriculture, household, industry or other activities.

A Agricultural fertilizer run-off is related to chemicals applied, farming practice and soil exchange capacity.

B Wastewaters primarily of domestic origin contain major amounts of P from:

1 Human, animal and plant residues

2 Surfactants (cleaning agent) discharge

3 Microbial and other cell masses

C Wastewaters primarily of industrial origin contain P related to:

1 Corrosion control

2 Scale control additives

3 Surfactants or dispersants

4 Chemical processing of materials including P

5 Liquors from clean-up operations of dusts, fumes, stack gases, or other discharges

III Phosphorus terminology is commonly confused because of the interrelations among biological, chemical, engineering, physical, and analytical factors.

A Biologically, phosphorus may be available as a nutrient, synthesized into living mass, stored in living or dead cells, agglomerates, or mineral complexes, or converted to degraded materials.

B Chemically, P exists in several mineral and organic forms that may be converted from one to another under favorable conditions. Analytical estimates are based upon physical or chemical techniques necessary to convert various forms of P into ortho phosphates which alone can be quantitated in terms of the molybdenum blue colorimetric test.

C Engineering interest in phosphorus is related to the prediction, treatment, or control of aqueous systems to favor acceptable water quality objectives. Phosphorus removal is associated with solids removal.

D Solubility and temperature are major physical factors in phosphorus behavior. Soluble P is much more available than insoluble P for chemical or biological transformations and the rate of conversion from one to another is strongly influenced by temperature.

E Table 1 includes a classification of the four main types of chemical P and some of the relationships controlling solubility of each group. It is apparent that no clear-cut separation can be made on a solubility basis as molecular weight, substituents and other factors affect solubility.

F Table 2 includes a scheme of analytical differentiation of various forms of P based upon:

1 The technique required to convert an unknown variety of phosphorus into ortho P which is the only one quantitated by the colorimetric test.

2 Solubility characteristics of the sample P or more precisely the means required to clarify the sample.

a Any clarification method is subject to incomplete separation. Therefore, it is essential to specify the method used to interpret the yield factor of the separation technique. The degree of separation of solubles and insolubles will be significantly different for:

1 Membrane filter separation (0.5 micrometer pore size)

2 Centrifugation (at some specified rpm and time)

3 Paper filtration (specify paper identification)

4 Subsidence (specify time and conditions)

G Analytical separations (Table 2) like those in Table 1, do not give a precise separation of the various forms of P which may be included quantitatively with ortho or poly P. Conversely some of the poly and organic P will be included with ortho P if they have been partially hydrolyzed during storage or analysis. Insolubles may likewise be included as a result of poor separation and analytical conditions.

1 The separation methods provide an operational type of definition adequate in most situations if the "operation" is known. Table 2 indicates the nature of incidental P that may appear along with the type sought.

Table 1

PHOSPHORUS COMPOUNDS CLASSIFIED BY CHEMICAL AND SOLUBILITY RELATIONS

Form	Water Soluble(1)	Insoluble(1)
1. Ortho phosphates $(PO_4)^{-3}$	Combined with monovalent cations such as H^+, Na^+, K^+, NH_4^+	Combined with multi valent cations such as Ca^{+2} Al^{+3} Fe^{+3}
2. Poly phosphates $(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$ $(P_3O_9)^{-3}$ and others depending upon the degree of dehydration.	as in 1 above Increasing dehydration decreases solubility	(a) as in 1 above (b) multi P polyphosphates (high mol. wt.) including the "glassy" phosphates
3. Organic phosphorus R-P, R-P-R (2) (unusually varied nature)	(a) certain chemicals (b) degradation products (c) enzyme P (d) phosphorylated nutrients	(a) certain chemicals (b) cell mass, may be colloidal or agglomerated (c) soluble P sorbed by insoluble residues
4. Mineral phosphorus	(a) as in 1 above	(a) as in 1 above (b) as in 2 above (c) geological P such as phosphosilicates (d) certain mineral complexes.

(1) Used in reference to predominance under common conditions.

(2) R represents an organic radical, P represents P, PO_4^{-3}, or its derivatives.

---

2 Total P in Table 2 includes liquid and separated residue P that may exist in the whole sample including silt, organic sludge, or hydrosoils. This recognizes that the feedback of soluble P from deposited or suspended material has a real effect upon the kinetics of the aqueous environment.

Table 2

PHOSPHORUS COMPOUNDS CLASSIFIED BY ANALYTICAL METHODOLOGY

Desired P Components	Technique(1)	Incidental P Included(2)
1. Ortho phosphates	No treatment on clear samples	Easily hydrolyzed (a) poly phosphates - (b) organic -P, - (c) Mineral -P, + or -
2. Polyphosphates (2)-(1) = poly P (hydrolyzable)	acid hydrolysis on clear samples, dilute (a) H_2SO_4 (b) HCl heated	(a) ortho-P + (b) organic -P + or - (c) mineral -P + or -
3. Organic phosphorus (3) - (2) + org P (hydrolyzable)	acid + oxidizing hydrolysis on whole sample. dilute (a) $H_2SO_4 + HNO_3$ (b) $H_2SO_4 + (NH_4)_2S_2O_8$ heated	(a) ortho P + (b) poly P + (c) mineral P + or -
4. Soluble phosphorus (preferably classified by clarification method)	clarified liquid following filtration, centrifugation or subsidence	generally includes (a) 1, 2, or 3 (b) particulates not completely separated
5. Insoluble phosphorus (residue from clarification)	Retained residues separated during clarification See (6)	(a) generally includes sorbed or complexed solubles.
6. Total phosphorus	Strong acid + oxidant digestion (a) $H_2SO_4 + HNO_3$ (b) $H_2SO_4 + HNO_3 + HClO_4$ (c) $H_2O_2 + Mg(NO_3)_2$ fusion	all components in 1, 2, 3, 4, 5 in the whole sample

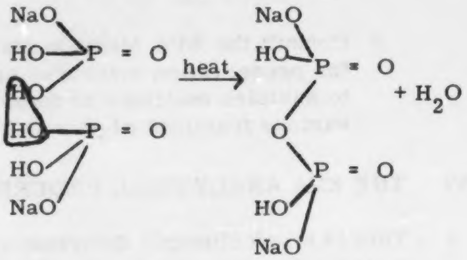
(1) Determinative step by phospho molybdate colorimetric method.

(2) Coding: + quantitative yield
- a small fraction of the amount present
+ or - depends upon the individual chemical and sample history

IV Polyphosphates are of major interest in cleaning agent formulation, as dispersants, and for corrosion control.

A They are prepared by dehydration of ortho phosphates to form products having two or more phosphate derivatives per molecule.

1 The simplest polyphosphate may be prepared as follows:



mono sodium ortho phosphate (2) disodium dihydrogen polyphosphate

2 The general form for producing polyphosphates from mono substituted orthophosphates is:

$$n\ (NaH_2PO_4) \xrightarrow[200-400^{\circ} C]{heat} (NaPO_3)_n + n\ H_2O$$

3 Di-substituted ortho phosphates or mixtures of substituted ortho phosphates lead to other polyphosphates:

$$2Na_2HPO_4 + NaH_2PO_4 \xrightarrow{heat} Na_5P_3O_{10} + 2H_2O$$

disodium hydrogen ortho phosphate + mono sodium di hydrogen ortho phosphate → pentasodium tri-phosphate + water

4 The polyphosphate series usually consist of the polyphosphate anion with a negative charge of 2 to 5. Hydrogen or metals commonly occupy these sites. The polyphosphate can be further dehydrated by heat as long as hydrogen remains. Di or trivalent cations generally produce a more insoluble polyphosphate than the same cation in the form of insoluble ortho phosphate. Insolubility increases with the number of P atoms in the polyphosphate. The "glassy" polyphosphates are a special group with limited solubility that are used to aid corrosion resistance in pipe distribution systems and similar uses.

B Polyphosphates tend to hydrolyze or "revert" to the ortho P form by addition of water. This occurs whenever polyphosphates are found in the aqueous environment.

1 The major factors affecting the rate of reversion of poly to orthophosphates include:

a) Temperature, increased T increases rate

b) pH, lower pH increases rate

c) Enzymes, hydrolase enzymes increase rate

d) Colloidal gels, increase rate

e) Complexing cations and ionic concentration increase rate

f) Concentration of the polyphosphate increases rate

2 Items a, b and c have a large effect upon reversion rate compared with other factors listed. The actual reversion rate is a combination of listed items and other conditions or characteristics.

3 The differences among ortho and ortho + polyphosphates commonly are close to experimental error of the colorimetric test in stabilized surface water samples. A significant difference generally indicates that the sample was obtained relatively close to a source of polyphosphates and was promptly analyzed. This implies that the reversion rate of polyphosphates is much higher than generally believed.

V SAMPLING AND PRESERVATION TECHNIQUES

A Sampling

1 Great care should be exercised to exclude any benthic deposits from water samples.

2 Containers should be cleaned in the same manner as labware (see VI. B. 1. below).

3 Certain plastic containers may be used. Possible adsorption of low concentrations of phosphorus should be checked.

4 If a differentiation of phosphorus forms is to be made, filtration should be carried out immediately upon sample collection. A membrane filter of 0.45 μm pore size is recommended for reproducible separations.

B Preservation

1 If at all possible, samples should be analyzed on the day of collection. At best, preservation measures only retard possible changes in the sample.

a Possible physical changes include solubilization, precipitation, absorption on or desorption from suspended matter.

b Possible chemical changes include reversion of poly to ortho P and decomposition of organic or mineral P.

c Possible biological changes include microbial decomposition of organic P and algal or bacterial growth forming organic P.

2 If it is impossible to do total phosphorus determinations on the day of collection, refrigerate at 4°C and add 2 ml concentrated H_2SO_4 per liter. Limit of holding for samples thus preserved is 24 hours. (6)

a Refrigeration decreases hydrolysis and reaction rates and also losses due to volatility.

b Sulfuric acid limits biological changes.

c Mercuric chloride also limits biological changes, but interferes with the analytical procedure if the chloride level is less than 50 mg Cl/liter. (See VI B. 2. below). Disposal of mercury-containing test wastes also adds time to the procedure.

3 Consult the EPA Methods Manual$^{(6)}$ for preservation measures applicable to samples collected to determine various fractions of phosphorus.

VI THE EPA ANALYTICAL PROCEDURE$^{(6)}$

A This is a colorimetric determination, specific for orthophosphate. Depending on the nature of the sample and on the type of data sought, the procedure involves two general operations:

1 Conversion of phosphorus forms to soluble orthophosphate (See Fig. 1):

a sulfuric acid-hydrolysis for polyphosphates, and some organic P compounds,

b persulfate digestion for organic P compounds.

2 The color determination involves reacting dilute solutions of phosphorus with ammonium molybdate and potassium antimonyl tartrate in an acid medium to form an antimony-phosphomolybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the orthophosphate concentration.

Color absorbance is measured at 880 nm or 650 nm and a concentration value obtained using a standard curve.

Reagent preparation and the detailed procedure can be found in the EPA manual.

The methods described there are usable in the 0.01 to 0.5 mg/liter phosphorus range. This range can be extended by dilution of samples.

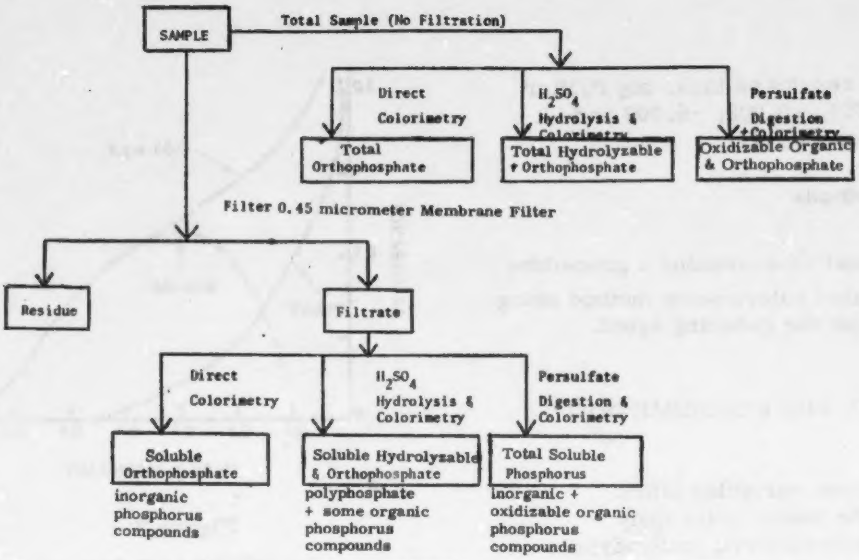

SAMPLE
Total Sample (No Filtration)
Direct Colorimetry
H_2SO_4 Hydrolysis & Colorimetry
Persulfate Digestion +Colorimetry
Total Orthophosphate
Total Hydrolyzable + Orthophosphate
Oxidizable Organic & Orthophosphate
Filter 0.45 micrometer Membrane Filter
Residue
Filtrate
Direct Colorimetry
H_2SO_4 Hydrolysis & Colorimetry
Persulfate Digestion & Colorimetry
Soluble Orthophosphate
Soluble Hydrolyzable & Orthophosphate
Total Soluble Phosphorus
inorganic phosphorus compounds
polyphosphate + some organic phosphorus compounds
inorganic + oxidizable organic phosphorus compounds

FIGURE 1
ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

B Interferences

1 Erroneous results from contaminated glassware is avoided by cleaning it with hot 1:1 HC1, treating it with procedure reagents and rinsings with distilled water. Preferably this glassware should be used only for the determination of phosphorus and protected from dust during storage. Commercial detergents should never be used.

2 Low total phosphorus values have been reported because of possible adsorption of phosphorus on iron, aluminum, manganese or other metal precipitates formed in wastewater samples.

a After digestion, adjust the pH of the sample to 7.0 ± 0.2 with 1N NaOH using a pH meter. If sample is not clear, add 2-3 drops 11N H_2SO_4 and filter.

b Filter through phosphorus-free 0.45 micrometer pore size cellulose filter. See Standard Methods, (7) page 472 about washing filters before use, since the discs can introduce significant phosphorus contamination.

3 The total phosphorus procedure requires a pH adjustment with a pH meter. Buffers made with phosphates are used to calibrate the meter in the applicable range. The meter electrodes must be thoroughly flushed free of buffer before their use with phosphorus test solutions. Otherwise, significant phosphorus contamination will result.

4 Others have reported interference from arsenic, arsenates, chlorine, chromium, sulfides, nitrite, tannins, lignin and other minerals and organics at high concentrations.

C Precision and Accuracy[6]

1 Organic phosphate - 33 analysts in 19 laboratories analyzed natural water samples containing exact increments of organic phosphate of 0.110, 0.132, 0.772, and 0.882 mg P/liter.

Standard deviations obtained were 0.033, 0.051, 0.130 and 0.128 respectively.

Accuracy results as bias, mg P/liter were: +0.003, +0.016, +0.023 and - 0.008, respectively.

2 Orthophosphate was determined by 26 analysts in 16 laboratories using samples containing orthophosphate in amounts of 0.029, 0.038, 0.335 and 0.383 mg P/liter.

Standard deviations obtained were 0.010, 0.008, 0.018 and 0.023 respectively.

Accuracy results as bias, mg P/liter were -0.001, -0.002, -0.009 and -0.007 respectively.

D Automated Methods

The EPA Manual also contains a procedure for the automated colorimetry method using ascorbic acid as the reducing agent.

VII VARIABLES IN THE COLORIMETRIC PROCEDURE

Several important variables affect formation of the yellow heteropoly acid and its reduced form, molybdenum blue, in the colorimetric test for P.

A Acid Concentration during color development is critical. Figure 2 shows that color will appear in a sample containing no phosphate if the acid concentration is low. Interfering color is negligible when the normality with respect to H_2SO_4 approaches 0.4.

1 Acid normality during color development of 0.3 to slightly more than 0.4 is feasible for use. It is preferable to control acidity carefully and to seek a normality closer to the higher limits of the acceptable range.

2 It is essential to add the acid and molybdate as one solution.

3 The aliquot of sample must be neutralized prior to adding the color reagent.

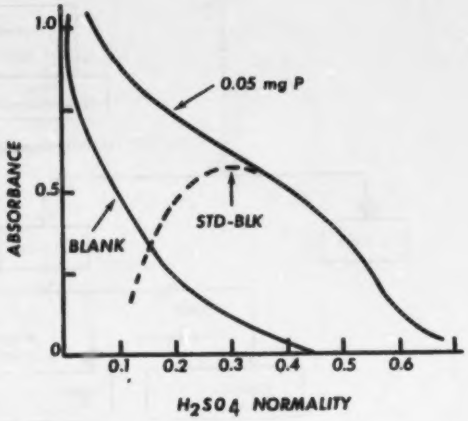


Figure 2

0-PHOSPHATE COLOR
VS ACIDITY

B Choice of Reductant - Reagent stability, effective reduction and freedom from deleterious side effects are the bases for reductant selection. Several reductants have been used effectively. Ascorbic acid reduction is highly effective in both marine and fresh water. It is the reductant specified in the manual NPDES procedure.

C Temperature affects the rate of color formation. Blank, standards, and samples must be adjusted to the same temperature (± 1°C), (preferably room temperature), before addition of the acid molybdate reagent.

D Time for Color Development must be specified and consistent. After addition of reductant, the blue color develops rapidly for 10 minutes then fades gradually after 12 minutes.

VIII DETERMINATION OF TOTAL PHOSPHORUS

A Determination of total phosphorus content requires the acid-hydrolysis and persulfate treatments to convert all phosphorus forms to the test-sensitive orthophosphate form.

B Determining total phosphorus content yields the most meaningful data since the various forms of phosphorus may change from one form to another in a short period of time. (See part V, B1)

IX DEVELOPMENT OF A STANDARD PROCEDURE

Phosphorus analysis received intensive investigation; coordination and validation of methods is more difficult than changing technique.

A Part of the problem in methods arose because of changes in analytical objectives such as:

1 Methods suitable to gather "survey" information may not be adequate for "standards".

2 Methods acceptable for water are not necessarily effective in the presence of significant mineral and organic interference characteristic of hydrosoils, marine samples, organic sludges and benthic deposits.

3 Interest has been centered on "fresh" water. It was essential to extend them for marine waters.

4 Instrumentation and automation have required adaptation of methodology.

B Analysts have tended to work on their own special problems. If the method apparently served their situations, it was used. Each has a "favorite" scheme that may be quite effective but progress toward widespread application of "one" method has been slow. Consequently, many methods are available. Reagent acidity, Mo content, reductant and separation techniques are the major variables.

C The persulfate digestion and single reagent (ascorbic acid) method described in VI above is the only method currently listed in the Federal Register "List of Approved Procedures" for NPDES requirements.

ACKNOWLEDGMENT:

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This outline was prepared by Ferdinand J. Ludzack, former Chemist, National Training Center, and by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Chemical Analysis, Nutrients, Phosphates, Phosphorus, Phosphorus Compounds, Pollutant Identification, Sampling, Water Analysis, Water Pollution Sources.

CONTROL OF INTERFERING IONS IN FLUORIDE DETERMINATIONS

I The principal source of error in fluoride analysis(1) is the presence of interfering ions. This is particularly true in the colorimetric methods, as can be seen from Table I which lists some ions commonly found in water and their affect on the Standard Methods fluoride analyses.

A In colorimetric analysis, one of the mechanisms by which these ions cause error is the changing of the reaction rate. Since the determination is based on color development, variations in reaction rate cause variations in fluoride reading.

B Some ions complex with either fluoride, in all methods, or with zirconium, in the colorimetric methods. When fluoride is complexed, low results are obtained, and when zirconium is complexed, the intensity of color is altered.

C Chlorine bleaches out the colors of dyes, and must always be removed before the sample can be analyzed colorimetrically.

II Whenever the quantity of interfering ions in the water is sufficient to cause an error of 0.1 mg/L fluoride or more, or whenever the analysis is unknown, these interferences must be removed or their effects diminished by one of the following methods:

A If the interferences are known to be caused by chemicals added during treatment in the water plant, they may sometimes be avoided by appropriate selection of a sampling point within the plant.

B In some cases the water sample can be diluted to bring the level of an interfering ion below the critical point. This procedure is applicable only when the fluoride level is sufficiently high to permit accurate analysis on the diluted sample.

C When the identity of the interfering ion is known, it may be possible to select an analytical method which has adequate tolerance for that ion.

TABLE I. INTERFERENCES

Concentration of Substance, in mg/L, Required to Cause an Error of Plus or Minus 0.1 mg/L at 1.0 mg/L F.

	SPADNS	Electrode
Alkalinity	5,000 (-)	7,000 (+)
Aluminum	0.1 (-)*	3.0 (-)
Chloride	7,000 (+)	20,000 (-)
Iron	10 (-)	200 (-)
Hexametaphosphate	1.0 (+)	>50,000
Phosphate	16 (+)	>50,000
Sulfate	200 (+)	50,000 (-)
Chlorine	Must Be Completely Removed With Arsenite	> 5,000
Color & Turbidity	Must Be Removed or Compensated For.	-----

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*Above Figure is for Immediate Reading. Allowed to Stand Two Hours Tolerance is 3.0 mg/L. Four Hour Tolerance is 30 mg/L.

D When the composition of the unfluoridated water is known and constant, equivalent quantities of interfering ions can be added to the fluoride standards, thereby neutralizing the effect of those ions.

E In all other cases the water sample must be distilled. As can be seen from Table I, distillation will seldom be necessary when the electrode method is used.

III The principle of the distillation process is the conversion of fluoride to the volatile acid, H_2SiF_6, in the presence of sulfuric acid and silica (glass beads). The fluosilicic acid distills over, leaving most of the interfering ions behind.

A The apparatus used is illustrated in Figure 1. It consists of a distillation flask, connecting tube and condenser. For convenience, apparatus with ground-glass joints is used, but a simpler arrangement using rubber stoppers is satisfactory (Figure 2).

B The critical features of the apparatus are the diameter of the connecting tube, the immersion of the thermometer, and fit of stoppers and/or ground-glass joints.

1 The diameter of the connecting tube must be large enough to preclude the carryover of bubbles.

2 The thermometer must be positioned low enough so that it will always be immersed.

3 Stoppers and joints must be tight enough to prevent the loss of fluoride-containing vapor.

C The Distillation Procedure is Carried Out as Follows:

1 Prepare the still by placing 400 ml distilled water, some glass beads and then 200 ml concentrated acid in the flask. Add the acid slowly and stir thoroughly. After all the acid has been added, stir again until the mixture is homogeneous.

2 Connect the apparatus as shown in the drawing, start water through the condenser and begin heating slowly. If bumping occurs, the acid and water have not been mixed sufficiently. When boiling starts, heating may be increased.

3 Continue heating until the temperature reaches 180°C. Discard this distillate, since it contains traces of fluoride from the acid and glassware. This preliminary procedure also serves to adjust the acid-water ratio for subsequent distillations.

4 Allow the flask to cool until the temperature drops to 120° C or lower. Measure out a 300-ml sample and add it to the flask. Mix thoroughly.

5 Distill as before until the temperature reaches 180°C. Retain the distillate (there should be 300 ml) for colorimetric determinations.

D The distillation process must be carried out very carefully, since there are several possible sources of difficulty.

1 The flame under the distillation flask must never touch the sides of the flask above the liquid level. Superheating of the vapor results in high sulfate carryover which causes a sulfate interference.

2 All stopper and joints must fit tightly to prevent loss of fluoride.

3 Flask contents must be thoroughly mixed to prevent bumping.

4 Distillation must be stopped when the temperature reaches 180°C. Higher temperatures result in excessive sulfate carryover.

5 Silver sulfate, at the ratio of 5 mg/mg of Cl, should be added when high-chloride samples are distilled. The presence of silver inhibits the volatilization of HCl which, in sufficient quantity, could interfere with the fluoride determination.

6 When high-fluoride samples are distilled, repeat the distillation using 300 ml of distilled water. Analysis of the distillate will indicate how complete the fluoride recovery was. If substantial amounts of fluoride appear in the second distillate, add the quantity to that obtained initially and flush again. Quantities of less than 0.1 mg/L F (0.03 mg) may be disregarded.

7 Because of the simplicity of apparatus and procedure, the distillation procedure can be readily automated. Modifications include magnetic stirring and a thermostat which turns off a quartz heating mantle when the correct temperature has been reached.

Fig. 1 DISTILLATION APPARATUS

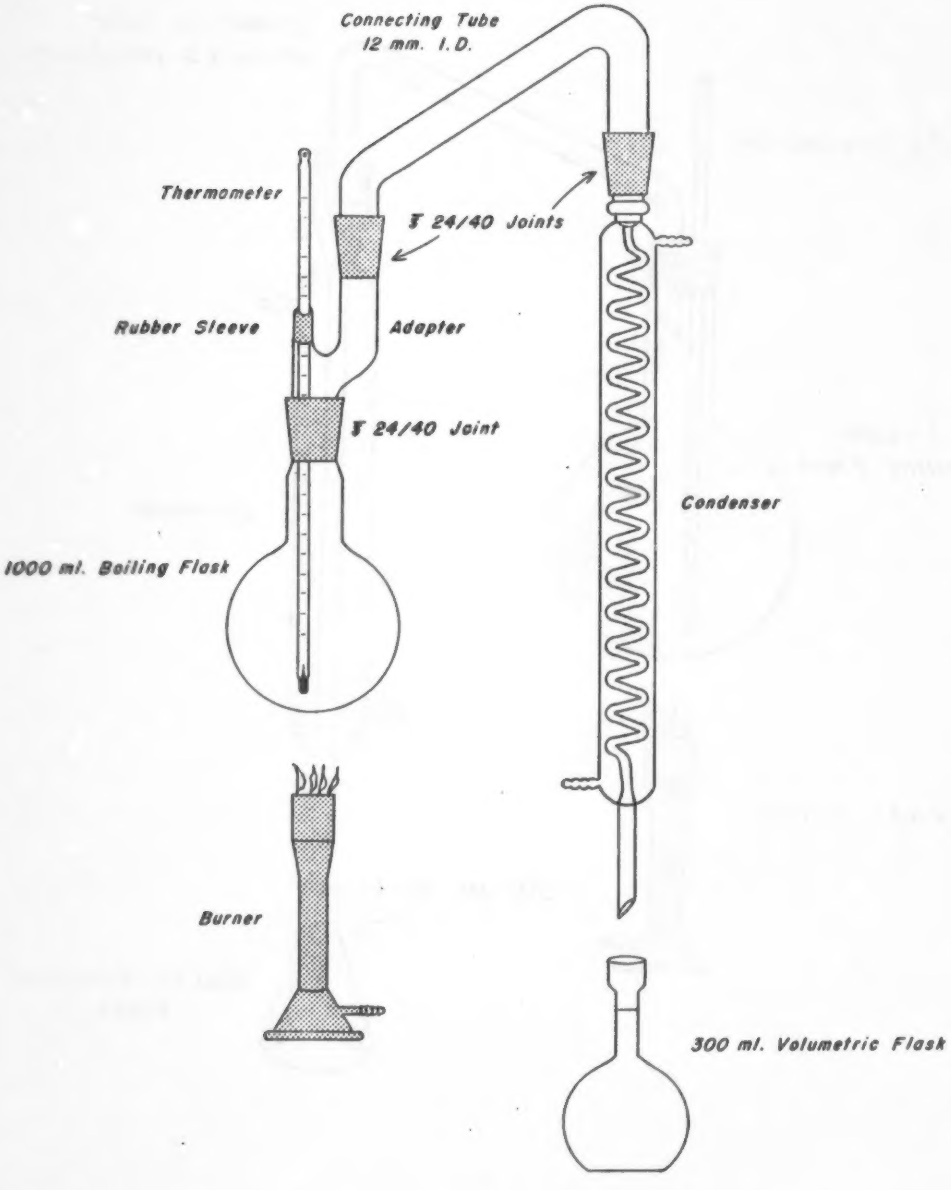
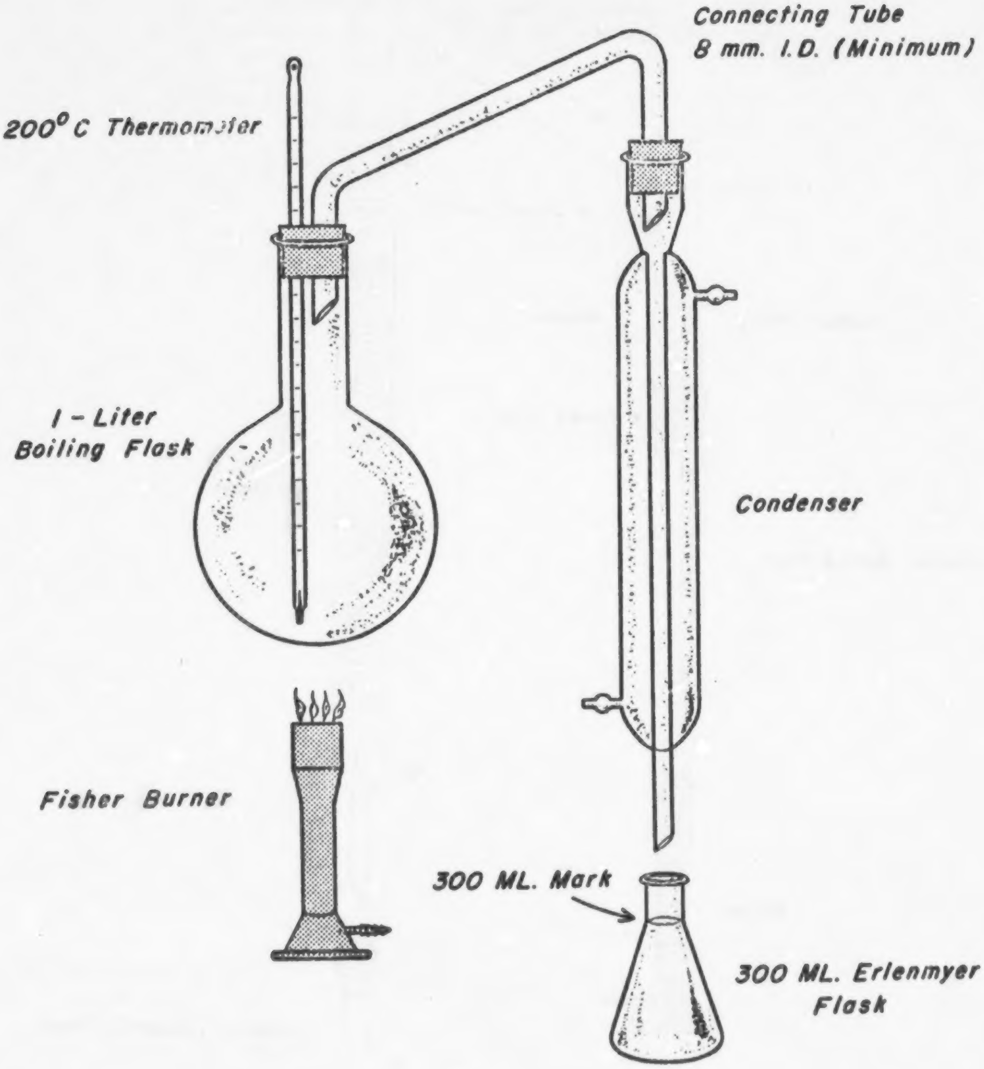

Connecting Tube
12 mm. I.D.
Thermometer
₮ 24/40 Joints
Rubber Sleeve
Adapter
₮ 24/40 Joint
Condenser
1000 ml. Boiling Flask
Burner
300 ml. Volumetric Flask

Fig. 2 SIMPLIFIED DISTILLATION APPARATUS


Connecting Tube
8 mm. I.D. (Minimum)
200° C Thermometer
1 - Liter
Boiling Flask
Condenser
Fisher Burner
300 ML. Mark
300 ML. Erlenmyer
Flask

IV COMPLIANCE METHODOLOGY

A NPDES/Certifications

Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary. However, manual distillation will be required to resolve any controversies.

Either an ion electrode or the SPADNS method may be used for the fluoride determination. The automated complexone method is also approved.

B Drinking Water

The ion electrode, the SPADNS, the automated complexone and the eriochrome cyanine R methods are all approved for drinking water samples.

Preliminary distillation is required for the SPADNS and the eriochrome cyanine R methods. It is an integral part of the automated complexone method. Distillation is not required if the ion electrode is used for drinking water samples.

REFERENCES

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3 Bellack, E. Simplified Fluoride Distillation Method. JAWWA 50:530. 1958.

This outline was prepared by Dr. E. Bellack, Office of Water Supply, EPA, Washington, D. C.

Descriptors: Analysis, Chemical Analysis, Fluoridation, Fluorides, Fluorine, Water Analysis.

AMMONIA, NITRITES AND NITRATES

I SOURCES AND SIGNIFICANCE OF AMMONIA, NITRITES AND NITRATES IN WATER

The natural occurrence of nitrogen compounds is best demonstrated by the nitrogen cycle (Figure 1).

A Ammonia

1 Occurrence

Ammonia is a product of the microbiological decay of animal and plant protein. In turn, it can be used directly to produce plant protein. Many fertilizers contain ammonia.

2 Significance

The presence of ammonia nitrogen in raw surface waters might indicate domestic pollution. Its presence in waters used for drinking purposes may require the addition of large amounts of chlorine in order to produce a free chlorine residual. The chlorine will first react with ammonia to form chloramines before it exerts its full bactericidal effects (free chlorine residual).

B Nitrites

1 Occurrence

Nitrite nitrogen occurs in water as an intermediate stage in the biological decomposition of organic nitrogen. Nitrite formers (nitrosomonas) convert ammonia under aerobic conditions to nitrites. The bacterial reduction of nitrates can also produce nitrites under anaerobic conditions. Nitrite is used as a corrosion inhibitor in industrial process water.

2 Significance

Nitrites are usually not found in surface water to a great extent. The presence of large quantities indicates a source of wastewater pollution.

C Nitrates

1 Occurrence

Nitrate formers convert nitrites under aerobic conditions to nitrates (nitrobacter). During electrical storms, large amounts of nitrogen (N_2) are oxidized to form nitrates. Finally, nitrates can be found in fertilizers.

2 Significance

Nitrates in water usually indicate the final stages of biological stabilization. Nitrate rich effluents discharging into receiving waters can, under proper environmental conditions, cause stress to stream quality by producing algal blooms. Drinking water containing excessive amounts of nitrates can cause infant methemoglobinemia.

II PRESERVATION OF AMMONIA, NITRATE AND NITRITE SAMPLES(8)

A If the sample is to be analyzed for Ammonia, Nitrate or Nitrite, cool to 4°C and analyze within 24 hours (48 hours for nitrite).

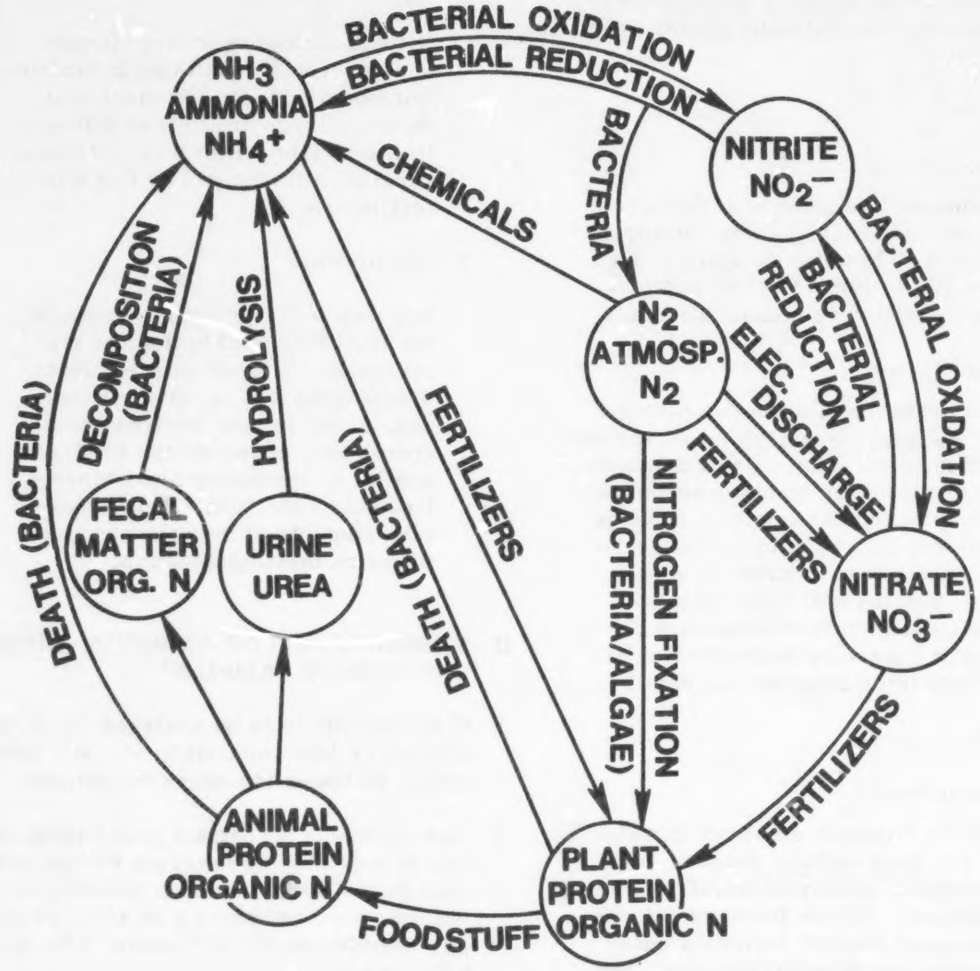
B For Ammonia or Nitrate plus Nitrite, the time can be extended by lowering the sample pH to less than 2 by the addition of concentrated sulfuric acid and storing at 4°C. (2 ml of acid per liter is usually sufficient. Check with pH paper).

C Mercuric chloride is effective as a preservative, but its use is discouraged because:

1 The Hg ion interferes with some of the nitrogen tests.

2 The Hg presents a disposal problem.

D Even when "preserved", conversion from one nitrogen form to another may occur. Samples should be analyzed as soon as possible.


NH3
AMMONIA
NH4+
BACTERIAL OXIDATION
BACTERIAL REDUCTION
NITRITE
NO2−
CHEMICALS
BACTERIA
N2
ATMOSP.
N2
BACTERIAL REDUCTION
BACTERIAL OXIDATION
ELEC. DISCHARGE
FERTILIZERS
NITRATE
NO3−
DECOMPOSITION (BACTERIA)
HYDROLYSIS
DEATH (BACTERIA)
DEATH (BACTERIA)
FERTILIZERS
FECAL MATTER ORG. N
URINE UREA
NITROGEN FIXATION (BACTERIA/ALGAE)
FERTILIZERS
ANIMAL PROTEIN ORGANIC N
PLANT PROTEIN ORGANIC N
FOODSTUFF

THE NITROGEN CYCLE

Figure 1

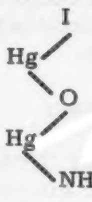
III DETERMINATION OF AMMONIA

A Nesslerization

1 Reaction

Nessler's reagent, a strong alkaline solution of potassium mercuric iodide, combines with NH_3 in alkaline solution to form a yellowish brown colloidal dispersion.

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow$$



$$+ 7KI + 2H_2O$$

Yellow-Brown

The intensity of the color follows the Beer-Lambert Law and exhibits maximum absorption at 425 nm.

2 Interferences

a Nessler's reagent forms a precipitate with some ions (e.g., Ca^{++}, Mg^{++}, Fe^{+++}, and $S^{=}$). These ions can be eliminated in a pretreatment flocculation step with zinc sulfate and alkali. Also, EDTA or Rochelle salt solution prevents precipitation with Ca^{++} or Mg^{++}.

b Residual chlorine indicates ammonia may be present in the form of chloramines. The addition of sodium thiosulfate will convert these chloramines to ammonia.

c Certain organics may produce an off color with Nessler's reagent. If these compounds are not steam distillable, the interference may be eliminated in the distillation method.

d Many organic and inorganic compounds cause a turbidity interference in this colorimetric test. Therefore direct nesslerization is not a recognized method. The following distillation procedure is a required, preliminary treatment.

B Distillation (6, 7, 8)

1 Reaction

a The sample is distilled in the presence of a borate buffer at pH 9.5

$$NH_4 + \xrightarrow{\Delta} NH_3 + H^+$$

$$H^+ + \underset{\text{Buffer}}{Na_2B_4O_7} \longrightarrow \text{pH 9.5 maintained}$$

b The ammonia in the distillate is then measured by either of two techniques.

1) Nesslerization is used for samples containing less than 1 mg/l of ammonia nitrogen.(6, 7, 8)

2) Absorption of NH_3 by boric acid and back titration with a standard strong acid is more suitable for samples containing more than 1 mg NH_3—N/l(6, 7, 8)

$$NH_3 + HBO_2 \longrightarrow NH_4{}^+ + BO_2{}^-$$

$$BO_2{}^- + H^+ \xrightarrow[+]{\text{Methyl Red}} HBO_2$$

Methylene Blue

pH 7.8 - 8.0	pH 6.8 - 7.0
Green	Purple

2 Interferences

a Cynate may hydrolyze, even at pH 9.5.

b Volatile organics may come over in the distillate, causing an off-color for Nesslerization. Aliphatic and aromatic amines cause positive interference by reacting in the acid titration. Some of these can be boiled off at pH 2 to 3 prior to distillation.

c Residual chlorine must be removed by pretreatment with sodium thiosulfate.

d If a mercury salt was used for preservation, the mercury ion must be complexed with sodium thiosulfate (0.2 g) prior to distillation.

3 Precision and Accuracy(8)

Twenty-four analysts in sixteen laboratories analyzed natural water samples containing the following amounts of ammonia nitrogen: 0.21, 0.26, 1.71, and 1.92 mg NH_3-N/liter.

a Precision

The standard deviation was: 0.122, 0.070, 0.244, and 0.279 mg NH_3-N/liter, respectively.

b Accuracy

The bias was: -0.01, -0,05, +0.01, and -0.04 mg NH_3-N/liter, respectively.

C Selective Ion Electrode(8)

1 Principle

A hydrophobic, gas-permeable membrane is used to separate the sample solution from an ammonium chloride internal solution. The ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

2 Interferences

a Volatile amines are a positive interference.

b Mercury forms a complex with ammonia so it should not be used as a preservative.

3 Precision and Accuracy

In a single laboratory (EPA) four surface water samples were analyzed containing the following amounts of ammonia nitrogen: 1.00, 0.77, 0.19, and 0.13 mg NH_3-N/liter.

a Precision

The standard deviations were 0.038, 0.017, 0.007, and 0.003 mg NH_3-N/liter, respectively.

b Accuracy

The % recovery on the 0.19 and 0.13 concentrations was 96% and 91% respectively.

D NPDES Ammonia Methodology

Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation is not necessary. However, manual distillation will be required to resolve any controversies.

Nesslerization, titration, and the selective ion electrode are all recognized methods. The automated phenolate method is also cited.

IV DETERMINATION OF NITRITE

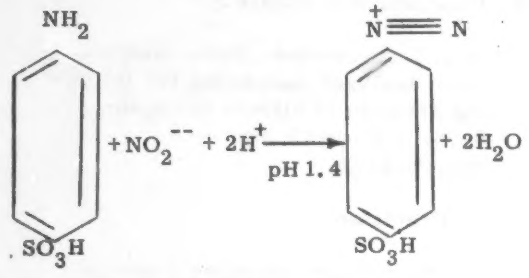
A Diazotization(6, 8)

1 Reaction

a Under acid conditions, nitrite ions react with sulfanilic acid to form a diazo compound.

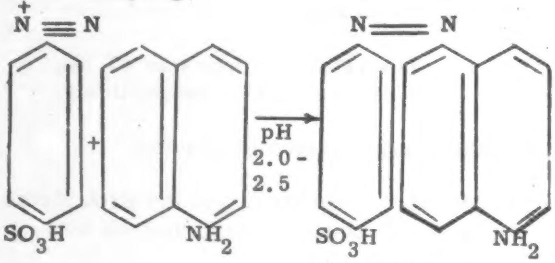
b The diazo compound then couples with α - naphthylamine to form an intense red azo dye which exhibits maximum absorption at 540 nm.

c Diazotization of Sulfanilamide



SULFANILIC ACID DIAZONIUM COMPOUND

d Coupling



intense red azo dye

2 Interferences

a There are very few known interferences at concentrations less than 1000 times that of nitrite.

b High alkalinity (greater than 600 mg/liter) will give low results due to a shift in pH.

c Strong oxidants or reductants in the sample also give low results.

3 Precision

On a synthetic sample containing 0.25 mg nitrite nitrogen/1, the ARS Water Minerals Study (1961) reported 125 results with a standard deviation of ± 0.029 mg/1.

B NPDES Nitrite Methodology

The colorimetric diazotization method, either manual or automated, is the only one cited in the Federal Register.

V DETERMINATION OF NITRATE

A Brucine Sulfate(6, 7, 8)

1 Reaction

Brucine sulfate reacts with nitrate in a 13N sulfuric acid solution to form a yellow complex which exhibits maximum absorption at 410 nm. Temperature control of the color reaction is extremely critical. The reaction does not always follow Beer's Law. However, a modification by Jenkins and Medsker(2) has been developed. Conditions are controlled in the reaction so that Beer's Law is followed for concentrations from 0.1 to 2 mg nitrate N/liter. The ideal range is from 0.1 to 1 mg NO_3-N/liter.

2 Interferences

a Nitrite may react the same as nitrate but can be eliminated by the addition of sulfanilic acid to the brucine reagent.

b Organic nitrogen compounds may hydrolyze and give positive interference at low (less than 1 mg/l) nitrate nitrogen concentrations. A correction factor can be determined by running a duplicate of the sample with all the reagents except the brucine-sulfanilic acid.

c Residual chlorine may be eliminated by the addition of sodium arsenite.

d Strong oxidizing or reducing agents interfere.

e The effect of salinity is eliminated by addition of sodium chloride to the blanks, standards and samples.

3 Precision and Accuracy(8)

a Twenty-seven analysts in 15 laboratories analyzed natural water samples containing the following increments of inorganic nitrate: 0.16, 0.19, 1.08 and 1.24 mg N/liter.

b Precision results as standard deviation were 0.092, 0.083, 0.245, and 0.214 mg N/liter respectively.

c Accuracy expressed as bias was -0.01, +0.02, +0.04 and +0.04 mg N/liter, respectively.

B Cadmium Reduction(6, 8)

1 Reaction

A non-turbid sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form an intensely colored azo dye which is measured spectrophotometrically.

To obtain the value for only nitrate, more of the non-turbid sample is tested using the same colorimetric reaction but without passing it through the reduction column. The resulting value represents the nitrite originally present in the sample. Subtracting this nitrite value for the non-reduced sample from the nitrate + nitrite value for the reduced sample gives the value for nitrate originally present in the sample.

2 Interferences

a Build-up of suspended matter in the reduction column will restrict sample flow. Filtration or flocculation with zinc sulfate should remove turbidity.

b High concentrations of iron, copper or other metals may interfere. EDTA is used to complex these.

c Large concentrations of oil and grease in a sample can coat the surface of the cadmium. Pre-extracting the sample with an organic solvent removes oil and grease.

3 Precision and accuracy(6)

In 11 laboratories, three samples were analyzed containing the following amounts of nitrate nitrogen: 0.05, 0.5, and 5 mg NO_3-N/liter.

a Precision

The relative standard deviation was 96.4%, 25.6%, and 9.2%, respectively.

b Accuracy

The relative error was 47.3%, 6.4%, and 1.0%, respectively.

4 Automated cadmium reduction

Standard Methods(6) and the EPA Methods Manual(8) contain details for the automated procedure.

C Hydrazine Reduction

A method using hydrazine to reduce nitrate to nitrite followed by subsequent measurement of nitrite by diazotization was reported by Fishman, et al.(1)

The means to determine nitrate is the same as above in the Cadmium Reduction Method. Subtraction of nitrite (determined from non-reduced sample) from the total nitrite (reduced nitrate + original nitrite) will give the original nitrate nitrogen concentration.

The procedure was adapted to the Auto Analyzer by Kamphake, et al.(3)
The method was revised in 1978 and printed in the EPA Methods Manual(8).

D Compliance Nitrate Methodology

1 NPDES/Certifications

The Federal Register lists the brucine sulfate, cadmium reduction and automated cadmium reduction or hydrazine reduction methods.

2 Drinking Water

The "Interim Primary Drinking Water Regulations; Amendments in the August 27, 1980 Federal Register page 57344 lists the brucine sulfate, cadmium reduction and automated cadmium reduction, and the automated hydrazine reduction methods as approved. Check this Federal Register for a list of the approved sources of the procedure to be followed for each method.

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6 Standard Methods for the Examination of Water and Waste Water. APHA. AWWA. WPCF. 14th Ed, 1976.

7 ASTM Book of Standards, Part 31, 1975.

8 Methods for Chemical Analysis of Water and Wastes, EPA-EMSL, Cincinnati, Ohio 45268, 1979.

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Descriptors: Ammonia, Chemical Analysis, Nitrates, Nitrites, Nitrogen, Nitrogen Compounds, Nitrogen Cycle, Nutrients, Water Analysis, Water Pollution Sources

TESTING FOR SOLIDS IN WATER SAMPLES

I INTRODUCTION

This outline presents the reasons why solids determinations are important to water quality improvement and a discussion of the various tests to obtain data for solids in water samples.

II SOLIDS AND WATER QUALITY

A Water Quality and Health Significance

The presence of solids affects the following:

1. Aesthetic quality of water
2. Aquatic life
3. Biological activity
4. Concentration of organic materials
5. Palatability of drinking water
6. Physiological reactions to drinking water

B Wastewater Treatment Plant (WWTP) Control Significance

Data obtained for solids is useful in determining:

1. Treatment requirements
2. Flow rate and loading information
3. Effectiveness of treatment processes
4. Oxygen demand
5. Quality of effluent

III SAMPLE HANDLING

A Containers

Use glass bottles or plastic containers that resist adsorption of particles onto walls.

B Preservation

Use no preservative. Cool at 4°C to minimize microbiological decomposition of solids.

C Holding Time-Analyze as soon as possible. Check about current maximum holding time for regulatory samples.

IV NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES) SOLIDS TESTS:

The various tests for solids are grouped under the title of "Residue" in the Federal Register "Guidelines Establishing Test Procedures for the Analysis of Pollutants".(1) The tests listed there are:

A Total Residue, mg/liter

Gravimetric 103-105°C(2)(3)

B Total dissolved (filterable) residue, mg/liter

Glass fiber filtration 180°C(2)(3)

C Total suspended (non-filterable) residue, mg/liter

Glass fiber filtration 103-105°C(2)(3)

D Settleable residue, ml/liter or mg/liter volumetric (2)(3) or gravimetric(3)

E Total volatile residue, mg/liter

Gravimetric 550°C(2)(3)

V SIGNIFICANCE OF TEST RESULTS

Tests for solids do not yield extremely accurate results. Interferences and sources of error are listed for each of the tests later in this outline.

Because there are so many variables, total solids and the various portions of solids are most practically defined in terms of the test conditions used for their determination. Using the term "residue" emphasizes that the data obtained is for matter which remains after applying treatments specified by a standard test procedure.

VI. GRAVIMETRIC METHODOLOGY FOR SOLIDS TESTS

All of the tests for solids are gravimetric. (Settleable solids may also be reported in terms of volume). Gravimetric methodology applied to solids involves weighing the residue that remains after the water in the sample has been separated from the solids either by evaporation or by filtration. The resulting residue should be completely dried before weighing. Its container is weighed before using, then weighed again while containing the residue. The difference in these weights is the weight of the residue.

A Containers

The choice of "containers" depends on the requirements of the test.

1 Evaporating dishes - these are used for total, total dissolved (filterable), and total volatile or volatile dissolved residues. They are to be made of porcelain, platinum or vycor. Dishes with a capacity of 100 ml are commonly used.

2 Glass fiber filter discs - these are used for total suspended (non-filterable), settleable, and volatile suspended residues. They are to be made of glass fibers and without organic binder. The discs are very fragile and must be handled carefully.

The diameter of the disc depends on the requirements of the filtration apparatus. Gooch crucibles or a funnel apparatus which includes a course (40-60 microns) fritted disc can be used as a support during filtration so 2.2 cm or 4.7 cm diameters are common disc sizes. For the dry-cool operations, a Gooch crucible or a planchet made of aluminum or stainless steel can be used to support the disc. (A watch glass can be used instead of the planchet).

The final weight is for a Gooch crucible containing a disc or else for a disc.

B Drying Temperatures

For NPDES testing, the temperature specified for the final drying of total and suspended residues is 103-105°C while the temperature specified for total dissolved residue is 180±2°C. The lower temperature is intended to facilitate the measurement of volatile substances while the higher is to measure anhydrous inorganic substances. This is in keeping with the intent of the different tests, i.e., to measure separate waste characteristics.

For a detailed discussion of the effect of different drying temperatures on results for these tests, see Standard Methods.(3)

C Check for Complete Drying

Three of the test procedures specify repeating the "drying cycle" until a constant weight is obtained.

The "drying cycle" consists of drying the residue separated from the sample (either by evaporation or filtration) in a drying oven at the temperature specified for the test. The residue in/on its container is next cooled to room temperature in a desiccator, then weighed on an analytical balance.

As a check on complete drying, the dry-cool-weigh steps are repeated and the weight is compared to the first weight obtained.

Ideally, the weights will be the same or within the balance error. However, each procedure specifies the maximum acceptable difference between the weights. If the difference exceeds this limit, the drying cycle is to be repeated and the second and third weights compared and so on until the check limit is satisfied.

If significant grease or oil is present in residues, it is difficult to completely dry them.

Experience with a particular test for samples from the same source enables an analyst to establish initial drying times that will accomplish complete drying and minimize the need for many repetitions of the drying cycle.

In some cases, using less sample volume is advantageous if incomplete drying is caused by too much residue which can entrap water.

VII. TOTAL RESIDUE

A Operational Definition

The matter remaining in an evaporating dish after evaporating off the water from a sample, then drying the material to constant weight at 103-105°C.

B Water Quality Effects

Total residue is originally dissolved or suspended in water. Some suspended matter will settle if the water is not greatly disturbed. The effect of solids on water quality often depends on which type it is. These effects are listed, then, under those headings.

Any of the forms of solids can demand oxygen and this affects the supply of oxygen available for aquatic life and natural decomposition processes.

C Wastewater Treatment Plant Control Significance

1 Loading criteria
2 Solids retention is a function of incoming solids to unit solids.

D Summary of Method(2)(3)

A well-mixed aliquot of the sample is quantitatively transferred to a preweighed evaporating dish and evaporated, then dried to constant weight at 103-105°C.

E Sample Volume

Choose an aliquot of sample sufficient to contain a residue of at least 25 mg.

F Interferences and/or Sources of Error

1 Ordinarily, non-representative particulates such as leaves, sticks, etc., are removed from the sample before processing it.

2 Floating oil and grease should be included in the sample and dispersed by a blender device before aliquoting.

3 If evaporation is conducted in a drying oven, lower the temperature to about 98°C during the initial process to prevent boiling and spattering of the sample. Final drying is done at 103-105°C.

4 Results are subject to negative error due to loss of volatile materials during evaporation.

G Check on Complete Drying

Dry to constant weight at 103-105°C. This entails repeating the drying cycle and comparing the weights obtained. The loss of weight should be less than 4% of the previous weight or 0.5 mg, whichever is less.

VIII. TOTAL DISSOLVED (FILTERABLE) RESIDUE

A Operational Definition

Those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

B Water Quality Effects

1 Public Water Supplies - taste, physiological effects, toxicity, corrosion

2 Irrigation - nutrient balance, toxicity, osmotic pressure

3 Livestock - taste, physiological effects, toxicity

4 Aquatic Life - nutrients, toxicity, osmotic pressure

Note: Bacteria can synthesize dissolved solids to suspended solids and also to settleable solids.

C Wastewater Treatment Plant Control Significance

1 Loading according to oxidation requirements.
2 Indication of possible agglomeration problems.

D Summary of Method(2)(3)

A well-mixed sample is filtered through a standard glass fiber filter. An aliquot of the filtrate is quantitatively transferred to a pre-weighed evaporating dish and evaporated, then dried to constant weight at 180°C.

E Sample Volume

Too much residue in the dish can crust over and entrap water that will not be driven off during drying. To help prevent this, a volume of sample yielding a maximum residue of 200 mg is suggested.

Specific conductance or ion exchange tests can be used to estimate a sample size with an appropriate concentration. (3)

F Interferences and/or Sources of Error

1 If evaporation is conducted in a drying oven, lower the temperature to about 98°C during the initial process to prevent boiling and spattering of the sample. Final drying is done at 180±2°C.

2 Hygroscopic components, e.g., Ca^{+2}, Mg^{+2}, Cl^{-1}, SO_4^{-2}, require prolonged drying and desiccation, followed by rapid weighing.

3 Bicarbonate component requires careful and prolonged drying to insure conversion to carbonate.

4 Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. This affects results.

G Check on Complete Drying

Dry to constant weight at 180±2°C, i.e., repeat the drying cycle until the weight loss is less than 0.5 mg.

IX. TOTAL SUSPENDED (NON-FILTERABLE) RESIDUE

A Operational Definition

Those solids which are retained by a glass fiber filter and dried to constant weight at 103-105°C.

B Water Quality Effects

1 Water Supplies - possible oxidation and/or agglomeration

2 Irrigation - plant growth and quality, soil quality, functioning of equipment

3 Recreation - Aesthetics

C Wastewater Treatment Plant Control Significance

1 Loading criteria for digesters according to possible oxygen demand
2 Check on clarifier efficiency
3 Balance of solids check
4 Settleability characteristics
5 Check on quality of effluent

D Requirements for National Pollutant Discharge Elimination System (NPDES)

1 All Secondary Treatment Plants

a The arithmetic average for effluent samples collected in a 30 consecutive day period shall not exceed 30 mg/liter.

b The arithmetic average for effluent samples collected in a 7 consecutive day period will not exceed 45 mg/liter.

c In a 30 consecutive day period, the average of the total suspended (non-filterable) solids in effluent samples shall not exceed 15% of the average of the total suspended solids in influent samples collected at approximately the same times. This constitutes 85% removal of such solids during the treatment process.

2 Waste Stabilization Ponds

These fall under special regulations if they are the sole process used for secondary treatment, if the maximum design capacity is two million gallons per day or less, and if operation and maintenance data indicate that the above requirements cannot be achieved.

The EPA Regional Administrator (or the State subject to EPA approval) is authorized to adjust the minimum levels so they conform to the suspended solids concentrations achievable with best waste stabilization pond technology. These levels vary with geographical locations.

E Summary of Method(2)(3)

A well-mixed sample is quantitatively transferred to a filtration apparatus and filtered through a pre-weighed glass fiber filter. The residue retained on the filter is dried to constant weight at 103-105°C.

F Sample Volume

The choice of volume is related to the size of the glass fiber filter used for the test. A volume that will yield at least 1.0 mg is cited in the EPA Methods Manual(2) for a 4.7 cm diameter filter, or else a weight of residue in the same proportion for other size filters. (For example, 0.47 mg for a 2.2 cm diameter filter).

The same manual(2) presents a scheme to estimate the volume of sample to use when the suspended solids content significantly affects the rate of the filtration procedure.

G Interferences and/or Sources of Error

1 Ordinarily, non-representative particulates such as leaves, sticks, etc., are removed from the sample before processing it.

2 Samples high in dissolved (filterable) solids may be subject to a positive interference. Exercise care in selecting the filter apparatus so that washing of the filter minimizes this potential interference.

3 The filter disc should be dried to constant weight (agreement within 0.5 mg) before use.

4. Consistent technique in carrying out the steps of the test as specified can control procedural variables which will affect results.

5 Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. This affects results.

H Check on Complete Drying

Dry to constant weight at 103-105°C, i.e., repeat the drying cycle until the weight loss is less than 0.5 mg.

X SETTLEABLE RESIDUE

A Operational Definition

That matter which will not stay in suspension during a one hour settling period.

B Water Quality Effects

1 Recreation - Aesthetics
2 Mechanical damages - affects navigation
3 Blanket effect destroys bottom fauna and biota, and spawning grounds. It also affects organic waste decomposition.
4 Organic components can deplete bottom oxygen and cause production of noxious gases like hydrogen sulfide.
5 Matter can adsorb metals and cause their concentration.

C Wastewater Treatment Plant Control Significance

1 Data can be used to check if flow rates are correct in aeration tanks.

2 Settleability characteristics, especially that of compaction, can be used to determine return-sludge rate and when to waste.

D Summary of Methods

1 Gravimetric[3]

The mg/liter of total suspended (non-filterable) residue is determined for the sample as described in IX E above.

Then the mg/liter non-settleable suspended residue is determined in the same manner, but on an aliquot of sample drawn from the middle of the supernatant in one liter of sample that has stood quiescent for one hour.

The mg/liter settleable matter is the difference between the total suspended and the non-settleable suspended residues.

2 Volumetric[3]

One liter of well-mixed sample is contained in an Imhoff Cone for a total of one hour. Then the volume of settled matter is recorded as ml/liter.

E Sample Volume

1 Gravimetric

a For the total suspended (non-filterable) residue, see IX F above.

b For the non-settleable suspended aliquot, the test specifies one liter or more of sample for the settling operation, and 250 ml of the resulting supernatant for processing.

2 Volumetric

One liter is specified.

F Interferences and/or Sources of Error

1 Provision must be made to ensure quiescence during the settling period.

2. Sample should not stand in sunlight.

G Check on Complete Drying

For the gravimetric method, the final residues are the suspended (non-filterable) residues on a filter disc. The drying cycle should be repeated until the weight loss is less than 0.5 mg.

XI TOTAL VOLATILE RESIDUE

A Operational Definition

That matter remaining after igniting a dried, total residue at 550°C in a muffle furnace for 15-20 minutes.

B Water Quality Effects

Matter that can undergo combustion has the potential to be oxidized. Such solids can cause dissolved oxygen depletion which affects aquatic life and natural organic waste decomposition.

C. Wastewater Treatment Plant Control Significance

This data provides:

1 A rough estimate of organic matter present
2 A monitor for treatment progress
3 A check on digester efficiency

D Summary of Method(3)

1 The dried, weighed residue obtained from the determination of total solids (VII D above) is ignited at 550°C in a muffle furnace for 15-20 minutes, then cooled and weighed. The difference in the weights before and after ignition is the total volatile residue.

2 A volatile residue ignition might also be applied to residues obtained from dissolved (filterable) or suspended (non-filterable) determinations. Such data is useful for treatment plant control.

E Sample Sizes

This test is performed on a dried, weighed residue resulting from one of the tests above (total, suspended or dissolved residues).

F Interferences and/or Sources of Error

1 Lack of control for the temperature of the muffle furnace

2 Residues are often very hygroscopic so weighings must be performed as soon as the container and residue are cool.

3 The principal source of error is failure to obtain a representative sample.

4 Loss of ammonium carbonate, water of crystallization, and/or loss of voliatile organic matter may occur during drying cycles prior to combustion.

5 There may be incomplete oxidation of certian complex organics, and decomposition of mineral salts during combustion.

6 Results should not be considered as an accurate measure of organic carbon, but may be useful as a control test in a wastewater treatment plant.

G Check on Drying to Constant Weight

The procedure(3) does not specify a check for constant weight when determining volatile residues.

1 Such residues are often very hygroscopic so it is difficult to obtain an accurate weight.

2 The data is not an extremely accurate measure of volatiles.

3 The data is usually used for control of waste treatment processes.

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Descriptors: Analytical Techniques, Chemical Analysis, Laboratory Tests, Solids

TURBIDITY

I INTRODUCTION

Turbidity as a water quality index refers to the degree of cloudiness present. Conversely, it is an index of clarity.

A Definition[1]

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through samples of water.

B Relationship to Suspended Solids

This optical property, turbidity, is caused by suspended matter. The size, shape and reflection/absorption properties of that matter (not its weight) determine the degree of optical effects. It is very possible to have water with high turbidity but very low mg/L suspended solids. Thus one cannot use turbidity results to estimate the weight concentration and specific gravity of the suspended matter.

C Causes

1 clay, sand

2 silt, erosion products

3 microscopic and macroscopic organisms

4 finely divided organic products

5 others

D Effects on Water Quality[2]

Turbidity is an indicator of possible suspended matter effects such as impeding effective chlorine disinfection and clogging fish gills. However, the following list is limited to those effects associated with the optical (clarity) nature of turbidity.

1 Reducing clarity in water

- a drinking water quality
- b food processing
- c industrial processes
- d fish (seeing natural food)
- e swimming/water sports

2 Obscuring objects in water

- a submerged hazards
- b water sports

3 Light penetration

- a affects depth of compensation point for photosynthetic activity (primary food production).

4 Thermal Effects

High turbidity causes near surface waters to become heated because of the heat absorbancy of the particulate matter.

- a Results in lower rate of oxygen transfer from air to water.
- b Stabilizes water column and prevents vertical mixing.
  - 1 decreases downward dispersion of dissolved oxygen
  - 2 decreases downward dispersion of nutrients

E Criteria for Standards[2]

1 Finished Drinking Water - Maximum of one unit where the water enters the distribution system.[3] The proposed standard is one unit monthly average and five units average of two consecutive days. Under certain conditions a five unit monthly average may apply at state option.

2 For Freshwater Aquatic Life and Wildlife - The combined effect of color and turbidity should not change the

compensation point more than 10% from its seasonally established norm, nor should such a change place more than 10% of the biomass of photosynthetic organisms below the compensation point.

3 Turbidity Criteria Used by Industries:

a Textiles - 0.3 to 5 units

b Paper and allied products - Ranges from 10 to 100 units, depending on type of paper.

c Canned, dried and frozen fruits and vegetables - Same as for finished drinking water (1 turbidity unit).

F Processes to Remove Turbidity (Solids)

1 Coagulation

a pre-chlorination enhances coagulation

2 Sedimentation

3 Filtration

4 Aeration

5 Others

II VISUAL METHODS TO ESTIMATE TURBIDITY

A Early Efforts

In the early 1900's, Whipple and Jackson measured turbidity and developed a calibration scale for turbidity instruments.

B Jackson Candle Turbidimeter

Later Jackson developed apparatus which utilized the same "extinction" principle as the instrument devised earlier with Whipple.

1 Instrument

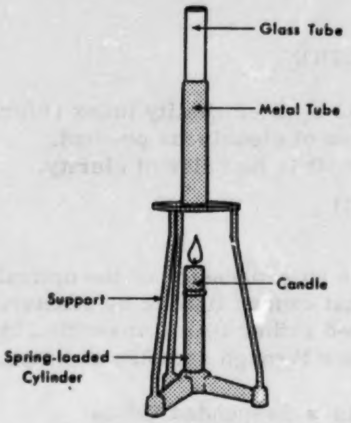

Figure 1 JACKSON CANDLE TURBIDIMETER

The sample was poured into a flat-bottomed, graduated glass tube held over a special candle. A turbidity reading was taken when the operator, observing from the top of the tube, saw the image of the candle flame disappear into a uniform glow. The reading related the final depth of sample in the tube with tube calibrations obtained from a standard suspension solution.

2 Standard Suspension

The standard was a suspension of silica prepared from Fuller's or diatomaceous earth. This was diluted to prepare a series of standard suspensions to graduate the turbidimeter. Graduations on all Jackson turbidimeters are made in conformity to this original data. Other suspensions are standardized by using the pre-calibrated turbidimeter and diluting accordingly.

3 Unit Used

Jackson Turbidity Unit (JTU) - parts per million suspended silica turbidity.

4 Standardization of Apparatus

The current edition of Standard Methods(1) contains specifications for the three essential components, i.e., the calibrated glass tube, the candle and a support.

5 Current Standard Suspension Solutions(1)

1 Natural turbid water from the same source as that tested gives best results. Determine turbidity with the instrument, then dilute to values desired.

2 The supernatant of a settled solution of kaolin is also used as a standard.

6 Limitations of Method

a Apparatus - difficult to exactly reproduce flame as to intensity and actual light path length. In general, it is a rather crude instrument with several variables that affect accuracy.

b Very fine suspended particles do not tend to scatter light of the longer wavelengths produced by the candle.

c Very dark and black particles can absorb enough light in comparison to the scattering of light to cause an incorrect reading of image extinction.

d Turbidities below 25 JTU cannot be directly measured. For lower turbidities (as in treated waters), indirect secondary methods are required to estimate turbidities.

C Hellige Turbidimeter(4)

This instrument utilizes the same extinction principle as the Jackson Candle Turbidimeter.

1 Equipment

An opal glass bulb supplies the light which is reflected (usually through a filter) upward through the sample which is contained in a glass tube. The entire system is enclosed in a black metal box. The operator views the sample by looking downward through an ocular tube screwed into the top of the box and adjusts the brightness of a central field of light by turning a calibrated dial on the outside of the apparatus. The point of uniform light intensity occurs when a black spot in the center of the field just disappears.

2 Range of Applicability

The equipment offers a choice of bulbs, filters and volumes of sample tubes. The variety affords a means to directly measure turbidity ranging from 0 through 150. The ranges can be extended by dilution.

3 Results

The final reading from the dial is translated into ppm silica turbidity units by using a graph corresponding to the bulb, filter and volume of sample used.

4 Standard Suspension Solution

Standardizing suspensions are not used by the operator. The graphs are supplied by the company for each instrument.

D Secchi Disk(5)

This is a very simple device used in the field to estimate the depth of visibility (clarity) in water.

1 Equipment

The disk is a weighted circular plate, 20 cm in diameter, with opposing black and white quarters painted on the surface. The plate is attached to a calibrated line by means of a ring on its center to assure that it hangs horizontally.

2 Readings

The disk is lowered into water until it disappears, lowered farther then raised until it reappears. The corresponding visibility depth (s) are determined from the calibrated line. Some read both depths and average them. Some read only the reappearance depth.

3 Standardizing the Procedure

There are many variables (position of sun and of observer, roughness of body of water, etc.) that affect readings. However, the same observer using a standard set of operating conditions can provide useful data to compare the visibility of different bodies of water.

4 Application of Results

Limnologists have found it convenient to establish a Secchi disk "factor" for estimating the photic depth where light intensity is about 1 per cent of full sunlight intensity. The true photic depth is determined by use of a submarine photometer and at the same time the observer takes a series of Secchi disk readings to obtain an average. Dividing the true photic depth by this average gives a factor which can be used to multiply other disk readings for an approximation of photic depth.

E Status of Visual Methods for Compliance Monitoring

The Federal Register(6) "List of Approved Methods" does not include any of these visual methods for National Pollutant Discharge Elimination System (NPDES) requirements. The visual methods are not recognized in the Federal Register(3) issue on Interim Drinking Water Regulations, either.

III NEPHELOMETRIC MEASUREMENTS FOR COMPLIANCE MONITORING

The subjectivity and apparatus deficiencies involved in visual methods of measuring turbidity make each unsuitable as a standard method.

Since turbidity is an expression of the optical property of scattering or absorbing light, it was natural that optical instruments with photometers would be developed for this measurement.

The type of equipment specified for compliance monitoring(3, 6) utilizes nephelometry.

A Basic Principle(7)

The intensity of light scattered by the sample is compared (under defined conditions) with the intensity of light scattered by a standard reference solution (formazin). The greater the intensity of scattered light, the greater the turbidity. Readings are made and reported in NTUs (Nephelometric Turbidity Units).

B Schematic

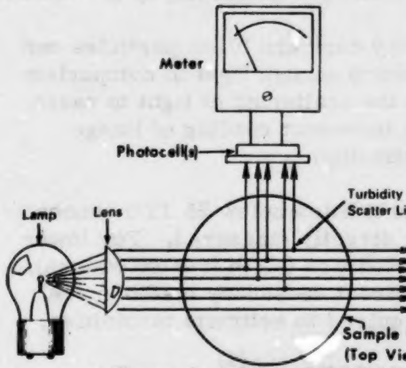

Figure 2 NEPHELOMETER (90° Scatter)

Light passes through a polarizing lens and on to the sample in a cell. Suspended particles (turbidity) in the sample scatter the light.

Photocell (s) detect light scattered by the particles at a 90° angle to the path of the incident light. This light energy is converted to an electric signal for the meter to measure.

1 Direction of Entry of Incident Light to Cell

a The lamp might be positioned as shown in the schematic so the beam enters a sample horizontally.

b Another instrument design has the light beam entering the sample (in a flat-bottom cell) in a vertical direction with the photocell positioned accordingly at a 90° angle to the path of incident light.

2 Number of Photocells

The schematic shows the photocell (s) at one 90 degree angle to the path of the incident light. An instrument might utilize more than one photocell position, with each final position being at a 90 degree angle to the sample liquid.

3 Meter Systems

a The meter might measure the signal from the scattered light intensity only.

b The meter might measure the signal from a ratio of the scattered light versus light transmitted directly through the sample to a photocell.

4 Meter Scales and Calbration

a The meter may already be calibrated in NTUs. In this case, at least one standard is run in each instrument range to be used in order to check the accuracy of the calibration scales.

b If a pre-calibrated scale is not supplied, a calibration curve is prepared for each range of the instrument by using appropriate dilutions of the standard turbidity suspension.

C EPA Specifications for Instrument Design(7)

Even when the same suspension is used for calibration of different nephelometers, differences in physical design of the turbidimeters will cause differences in measured values for the turbidity of the same sample. To minimize such differences, the following design criteria have been specified by the U. S. Environmental Protection Agency.

1 Defined Specifications

a Light Source

Tungsten lamp operated at a color temperature between 2200-3000°K.

b Distance Traveled by Light

The total of the distance traversed by the incident light plus scattered light within the sample tube should not exceed 10 cm.

c Angle of Light Acceptance of the Detector

Detector centered at 90° to the incident light path and not to exceed ± 30° from 90°.

The detector, and filter system if used, shall have a spectral peak response between 400 and 600 nm.

d Applicable Range

The maximum turbidity to be measured is 40 units. Several ranges will be necessary to obtain adequate coverage. Use dilution for samples if their turbidity exceeds 40 units.

2 Other EPA Design Specifications

a Stray Light

Minimal stray light should reach the detector in the absence of turbidity.

Some causes of stray light reaching the photocell (s) are:

a Scratches or imperfections in glass cell windows.

2 Dirt, film or condensation on the glass.

3 Light leakages in the instrument system.

A schematic of these causes is shown in Figure 3.

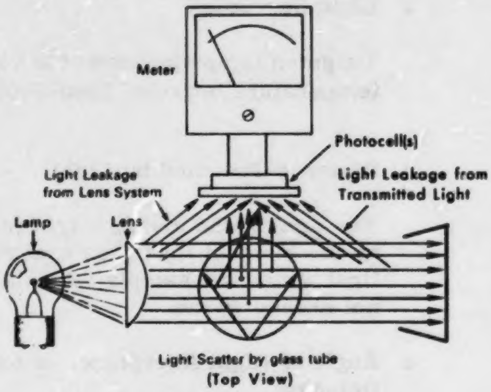
Meter
Photocell(s)
Light Leakage from Lens System
Light Leakage from Transmitted Light
Lamp
Lens
Light Scatter by glass tube (Top View)

Figure 3 NEPHELOMETER SOURCES OF STRAY LIGHT

Stray light error can be as much as 0.5 NTU. Remedies are close inspection of sample cells for imperfections and dirt, and good design which can minimize the effect of stray light by controlling the angle at which it reaches the sample.

b Drift

The turbidimeter should be free from significant drift after a short warm-up period. This is imperative if the analyst is relying on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges.

c Sensitivity

In waters having turbidities less than one unit, the instrument should detect turbidity differences of 0.02 unit or less. Several ranges will be necessary to obtain sufficient sensitivity for low turbidities.

3 Examples of instruments meeting the specifications listed in 1 and 2 above include:

a Hach Turbidimeter Model 2100 and 2100 A

b Hydroflow Instruments DRT 100, 200, and 1000

4 Other turbidimeters[12] meeting the listed specifications are also acceptable.

D Sources of Error

1 Marred Sample Cells

a Discard scratched or etched cells.

b Do not touch cells where light strikes them in instrument.

c Keep cells scrupulously clean, inside and out.[8]

1 Use detergent solution.

2 Organic solvents may also be used.

3 Use deionized water rinses.

4 Rinse and dry with alcohol or acetone.

2 Standardizing Suspensions[7]

a Use turbidity - free water for preparations. Filter distilled water through a 0.45 μ m pore size membrane filter if such filtered water shows a lower turbidity than the distilled water.

b Prepare a new stock suspension of Formazin each month.

c Prepare a new standard suspension and dilutions of Formazin each week.

3 Sample Interferences

a Positive

1 Finely divided air bubbles

b Negative

1 Floating debris

2 Coarse sediments (settle)

3 Colored dissolved substances (absorb light)

E Reporting Results(7)

NTU	Record to Nearest:
0.0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

F Precision and Accuracy(7)

1 In a single laboratory (MDQARL), using surface water samples at levels of 26, 41, 75 and 180 NTU, the standard deviations were ± 0.60, ± 0.94, ± 1.2 and ± 4.7 units, respectively.

2 Accuracy data is not available at this time.

IV STANDARD SUSPENSIONS AND RELATED UNITS(9)

One of the critical problems in measuring turbidity has been to find a material which can be made into a reproducible suspension with uniform sized particles. Various materials have been used.

A Natural Materials

1 Diatomaceous earth

2 Fuller's earth

3 Kaolin

4 Naturally turbid waters

Such suspensions are not suitable as reproducible standards because there is no way to control the size of the suspended particles.

B Other Materials

1 Ground glass

2 Microorganisms

3 Barium sulfate

4 Latex spheres

Suspensions of these also proved inadequate.

C Formazin

1 A polymer formed by reacting hydrazine sulfate and hexamethylenetetramine sulfate.

2 It is more reproducible than previously-used standards. Accuracy of ± one per cent for replicate solutions has been reported.

3 In 1958, the Association of Analytical Chemists initiated a standardized system of turbidity measurements for the brewing industry by:

a defining a standard formula for making stock Formazin solutions and

b designating a unit of measurement based on Formazin, i.e., the Formazin Turbidity Unit (FTU).

4 During the 1960's Formazin was increasingly used for water quality turbidity testing. It is the currently recognized standard for compliance turbidity measurements.

D Units

1 At first results were translated into Jackson Turbidity Units (JTU). However, the JTU was derived from a visual measurement using concentrations (mg/liter) of silica suspensions prepared by Jackson. They have no direct relationship to the intensity of light scattered at 90 degrees in a nephelometer.

2 For a few years, results of nephelometric measurements using specified Formazin standards were reported directly as Turbidity Units (TU's).

3 Currently, the unit used is named according to the instrument used for measuring turbidity. Specified Formazin standards are used to calibrate the instrument and results are reported as Nephelometric Turbidity Units (NTUs).

V TURBIDITY MEASUREMENTS FOR PROCESS CONTROL

The schematic and design characteristics discussed above for nephelometric instruments is the required method for measuring turbidity for compliance purposes. Turbidity data is also widely used to check water for process design purposes and to monitor water for process control purposes. The nature of the liquids to be monitored, and the degree of sensitivity required for signalling the remedy to be applied have led to the development of monitoring instrumentation that differs in design or in principle from the instrument previously described.

A Users of Control Data

1 Potable Water Treatment Plants

2 Municipal Wastewater Treatment Plants

3 Industrial Processers

B Applications of Control Data (10, 11)

1 Coagulation Processes

a To check the effectiveness of different coagulants.

b To check the effectiveness of different dosages.

c To regulate chemical dosages by automating chemical feed controls.

2 Settling Processes

a To determine intermittent need for settling processes.

b To control the sludge blanket height in activated sludge treatment processes.

c To activate removal and re-cycling of very high density sludge from settling tanks.

d To monitor effectiveness of settling processes.

3 Filtration Processes

a To determine intermittent need for filtration.

b To facilitate high rate filtration processes.

c To prevent excessive loadings for filtration systems.

d To check the efficiency of filtration systems.

e To regulate filter backwash operations.

4 Rust in Water Distribution Systems

a To locate sources of contamination.

b To monitor intermittent occurrences.

5 Steam Boiler Operations

a To detect corrosion products in boiler water.

b To detect evidences of corrosion in condensates.

c To determine the effectiveness of corrosion treatment measures.

C Varieties of Instrumentation

1 Surface Scatter Nephelometers

In forward - scattering instruments, the angle of the incident light is adjusted to illuminate the surface of a smooth flowing liquid at an angle of about 15 degrees from horizontal, rather than beamed through a glass cell of the liquid as described for a nephelometer earlier in this outline. A photocell is located immediately above the illuminated area so that vertically scattered light from turbidity in the sample reaches it.

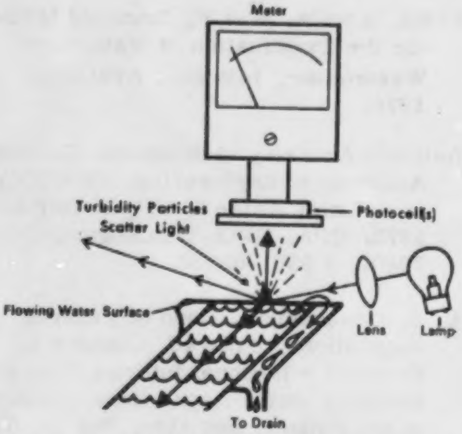

Figure 4 NEPHELOMETER (Surface Scatter)

Variations of the methodology include sidescatter and backscatter designs.

a Advantages

1 No glass sample cells are used. Attendant problems of cleanliness and condensation are eliminated. The surface of the liquid provides a near-perfect optical surface which is difficult to achieve in glass cells.

2 Stray light effects on the photocell are minimized because the simpler design eliminates some of the sources of stray light.

3 Since flowing sample is used, interferences from air bubbles and/or floating materials are quickly eliminated.

4 This design is sensitive to the presence of larger suspended particles.

b Disadvantage

As turbidity becomes high, penetration of incident light decreases to cause a falling off of response.

2 Absorption Spectrophotometry

The incident light is beamed through a smooth, flat stream of sample and the transmitted light (in contrast to nephelometric scattered light) is measured by a spectrophotometer. A schematic is shown in Figure 5.

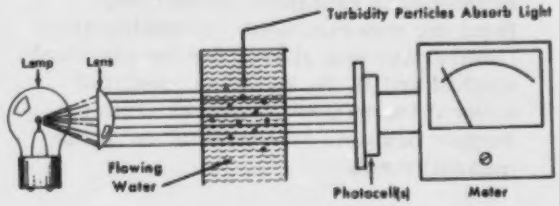

Figure 5 ABSORPTION SPECTROPHOTOMETRY

a Advantages

1 No glass sample cells are used.

2 The simpler design eliminates sources of stray light.

3 Applicable to measure high turbidities, e.g., in sludges.

b Disadvantage

1 Low sensitivity for many applications.

2 Color constituents interfere.

VI SUMMARY

Turbidity measurements represent the optical property of light scattering by suspended solids. NTUs are an index of the effects of the size, etc., of suspended particles but cannot be used to indicate mg/L quantities of those particles. The parameter is required for finished potable water and is extremely useful in reference to aesthetic quality (clarity), photic conditions and thermal effects in bodies of water. It is also widely applied for process control of water and wastewater treatment and of industrial processes.

There have been difficulties in developing a satisfactory standard method for this measurement. Early methods depended on a subjective judgement of an extinction point where transmitted light balanced scattered light in rather crude apparatus. Although the apparatus was refined and standardized to a large extent, the subjectivity of these visual methods was still an unsatisfactory element of such methodology.

Eventually, optical instrumentation was developed to eliminate subjectivity from the measurement. Nephelometry (scattering) was chosen for the standard method and U. S. EPA has specified several instrument design criteria to further promote standardization of the measurement.

Finding a suitable (reproducible) standard suspension has also been a problem. Currently, Formazin is specified as the standard because, to date, it is more reproducible than other suspensions proved to be.

Establishing a meaningful unit progressed along with development of instrumentation and agreement on a standard suspension. The current unit (NTU) is derived from the method of measurement, nephelometry, and use of a standard Formazin suspension.

Even with the efforts to standardize instrument design, to find a suitable standard suspension, and to agree on a meaningful unit, there are still problems about this measurement. Instruments meeting the design criteria and standardized with Formazin suspensions can give turbidity readings differing significantly for the same sample.

Another problem area is associated with sample dilutions. Work has indicated a progressive error on sample turbidities in excess of 40 units, so such samples are to be diluted. However, obtaining a dilution exactly representative of the original suspension is difficult to achieve. Thus dilutions often significantly fail to give linearly decreased results when re-measured.

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12 Bausch and Lomb, and Turner of California are additional examples (9/77) of models meeting the listed specifications.

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Descriptors: Chemical Analysis, Instrumentation, Secchi disks, Turbidity, Wastewater, Water Analysis

SPECIFIC CONDUCTANCE

I INTRODUCTION

An electrical conductivity measurement of a solution determines the ability of the solution to conduct an electrical current. Very concentrated solutions have a large population of ions and transmit current easily or with small resistance. Since resistivity is inversely related to conductivity $K = \frac{1}{R}$, a very concentrated solution has a very high electrical conductivity.

Electrical conductivity is determined by transmitting an electrical current through a given solution, using two electrodes. The resistance measured is dependent principally upon the ionic concentration, ionic charge, and temperature of the solution although electrode characteristics (surface area and spacing of electrodes) is also critical. Early experiments in standardizing the measurement led to construction of a "standard cell" in which the electrodes were spaced exactly 1 cm and each had a surface area of 1 cm^2. Using this cell, electrical conductivity is expressed as "Specific Conductance". Modern specific conductance cells do not have the same electrode dimensions as the early standard cell but have a characteristic electrode spacing/area ratio known as the "cell constant".

$$K_{sp} = \frac{1}{R} \times \frac{\text{distance (cm)}}{\text{area (cm}^2\text{)}}, \quad K_{sp} = \frac{1}{R} \times k$$

k = cell constant

Specific conductance units are Mhos/cm or reciprocal ohms/cm. Most natural, fresh waters in the United States have specific conductances ranging from 10 to 1,000 micromhos/cm. (1 micromho = 10^{-6} mho).

II CONDUCTIVITY INSTRUMENTS

Nearly all of the commercial specific conductance instruments are of a bridge circuit design, similar to a Wheatstone Bridge. Null or balance is detected either by meter movement, electron "ray eye" tubes, or headphones. Since resistance is directly related to temperature, some instruments have automatic temperature compensators, although inexpensive models generally have manual temperature compensation.

Conductivity instruments offer direct specific conductance readout when used with a cell "matched" to that particular instrument.

Electrodes within the cell may become damaged or dirty and accuracy may be affected; therefore, it is advisable to frequently check the instrument readings with a standard KCl solution having a known specific conductance.

III CONDUCTIVITY CELLS

Several types of conductivity cells are available, each having general applications. Dip cells are generally used for field measurement, flow cells for measurement within a closed system, and pipet cells for laboratory use. Many modifications of the above types are available for specialized laboratory applications; the Jones cells and inductive capacitance cells are perhaps the most common.

Examples of various cell ranges for the RB3 - Industrial Instruments model (0-50 micromhos/cm scale range) are in Table 1.

Cell Number	Relative Conductivity Value	Maximum range micromhos/cm	Most accurate range micromhos/cm
Cel VSO2	1	0 - 50	2 - 30
Cel VS2	10	0 - 500	20 - 300
Cel VS2O	100	0 - 5000	200 - 3000

Table 1

IV Computation of Calibration Constant

A calibration constant is a factor by which scale readings must be multiplied to compute specific conductance.

$K_{sp} = cM$

where K_{sp} = actual specific conductance

c = calibration constant

M = meter reading

For example, a 0.001 N KCl solution (147 micromhos/cm standard) may show a scale reading of 147.

$$147 = c\ 147,\ c = \frac{147}{147} = 1.00$$

In this case the cell is perfectly "matched" to the instrument, the calibration constant is 1.00, and the scale reading represents actual specific conductance. A variety of cells, each covering a specific range, may be used with any one instrument. However, a calibration constant for each cell must be computed before solutions of unknown specific conductance can be determined.

V RELATIONSHIP OF SPECIFIC CONDUCTANCE TO IONIC CONCENTRATION

Natural water consists of many chemical constituents, each of which may differ widely in ionic size, mobility, and solubility. Also, total constituent concentration and proportions of certain ions in various natural waters range considerably. However, it is surprising that for most natural waters having less than 2,000 mg/L. dissolved solids, dissolved solids values are closely related to specific conductance values, ranging in a ratio of .62 to .70. Of course this does not hold true for certain waters having considerable amounts of nonionized soluble materials, such as organic compounds and nonionized, colloidal inorganics.

Properties of some inorganic ions in regard to electrical conductivity are shown below:

Ion	micromhos/cm per meq/L conc.
Calcium	52.0
Magnesium	46.6
Sodium	48.9
Potassium	72.0
Bicarbonate	43.6
Carbonate	84.6
Chloride	75.9

VI ESTIMATION OF CONSTITUENT CONCENTRATIONS

Generally speaking, for waters having a dissolved solids concentration of less than 1,000 mg/L, calcium and magnesium (total hardness), sodium, bicarbonate and carbonate (total alkalinity), and sulfate are the principal or most abundant ions, representing perhaps 90-99% of the total ionic concentration of the water. Specific conductance, total hardness and total alkalinity are all simple and expedient measurements which can be performed in the field. Therefore, the remaining principal ions are sodium and sulfate, and concentrations of these can be estimated by empirical methods. For example, we find that a certain water has:

K_{sp} = 500 micromhos/cm
Total Hardness = 160 mg/L or 3.20 meq/L
Total Alkalinity = 200 mg/L or 3.28 meq/L, as bicarbonate.

Next we multiply the specific conductance by *0.011 ($500 \times 0.011 = 5.50$) to estimate the total ionic concentration in meq/L.

---

* This factor may vary slightly for different waters

Cations (meq/L)		Anions (meq/L)	
Calcium	3.20	Carbonate	0.00
Magnesium		Bicarbonate	3.28
Sodium	5.50-3.20 = 2.30	Sulfate	5.50-3.28 = 2.22
Total Cations	5.50	Total Anions	5.50

Realizing that several variables are involved in empirical analysis, application rests entirely upon testing the formula with previous complete laboratory analyses for that particular water. If correlation is within acceptable limits, analytical costs may be substantially reduced. Empirical analysis can also be used in determination of proper aliquots (dilution factor) necessary for laboratory analysis.

Records of laboratory chemical analysis may indicate that a particular stream or lake shows a characteristic response to various streamflow rates or lake water levels. If the water's environment has not been altered and water composition responds solely to natural causes, a specific conductivity measurement may be occasionally used in substitution for laboratory analyses to determine water quality. Concentration of individual constituents can thus be estimated from a specific conductance value.

VII APPLICATIONS FOR SPECIFIC CONDUCTANCE MEASUREMENTS

A Laboratory Operations(2)

1 Checking purity of distilled and deionized water

2 Estimation of dilution factors for samples

3 Quality control check on analytical accuracy

4 An electrical indicator

B Agriculture

1 Evaluating salinity

2 Estimating Sodium Adsorption Ratio

C Industry(3)

1 Estimating corrosiveness of water in steam boilers

2 Efficiency check of boiler operation

D Geology

1 Stratigraphic identification and characterization

a geological mapping
b oil explorations

E Oceanography

1 Mapping ocean currents

2 Estuary studies

F Hydrology

1 Locating new water supplies

a buried stream channels (See Fig. 1)
b springs in lakes and streams (See Fig. 2)

2 Detection and regulation of sea water encroachment on shore wells

G Water Quality Studies

1 Estimation of dissolved solids(2) (See Section V, also Fig. 3)

2 Empirical analysis of constituent concentrations (See Section VI, also reference 2)

3 Quality control check for salt water conversion studies

4 Determination of mixing efficiency of streams (See Fig. 4)

5 Determination of flow pattern of polluted currents (See Fig. 4)

6 Identification of significant fluctuations in industrial wastewater effluents.

7 Signal of significant changes in the composition of influents to waste treatment plants

FIGURE 1

DETECTION OF BURIED STREAM CHANNELS

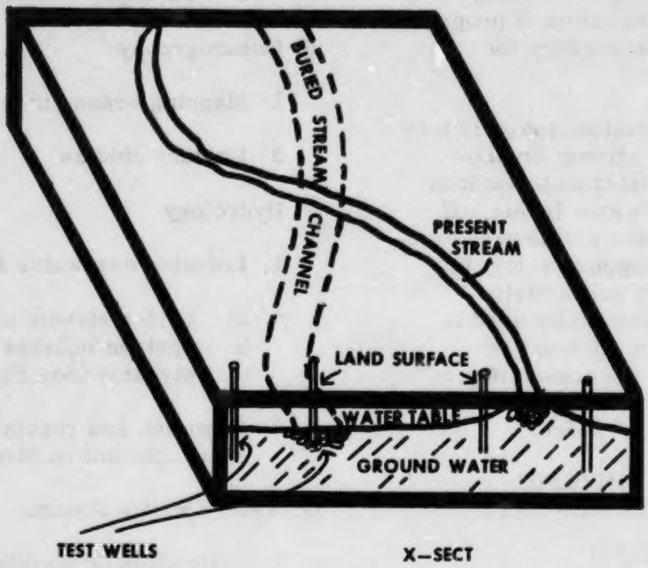
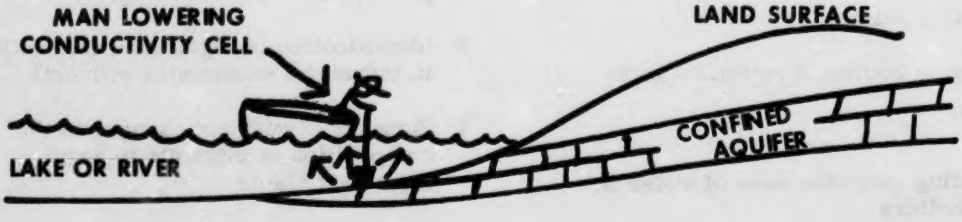

BURIED STREAM CHANNEL
PRESENT STREAM
LAND SURFACE
WATER TABLE
GROUND WATER
TEST WELLS
X–SECT

FIGURE 2

DETECTION OF SPRINGS IN LAKES AND STREAMS


MAN LOWERING CONDUCTIVITY CELL
LAND SURFACE
CONFINED AQUIFER
LAKE OR RIVER

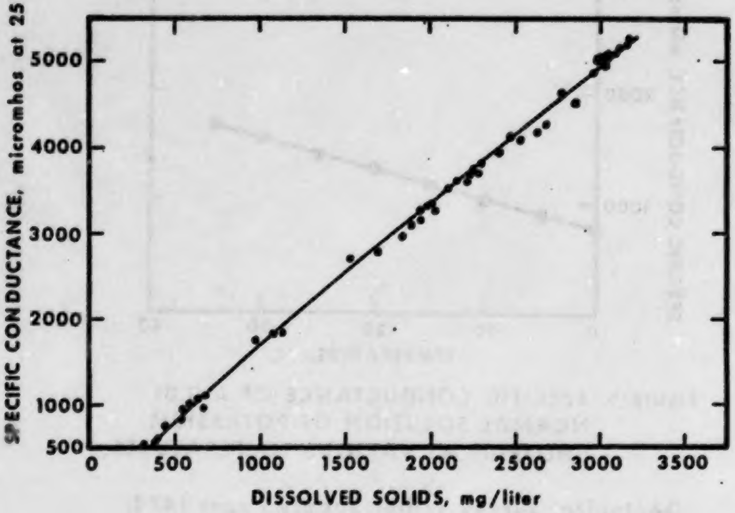


Figure 3. SPECIFIC CONDUCTANCE AND DISSOLVED SOLIDS IN COMPOSITES OF DAILY SAMPLES. , GILA RIVER AT BYLAS, ARIZONA, OCTOBER 1, 1944 TO SEPTEMBER 30, 1944.

Geological Survey Water-Supply Paper 1473.

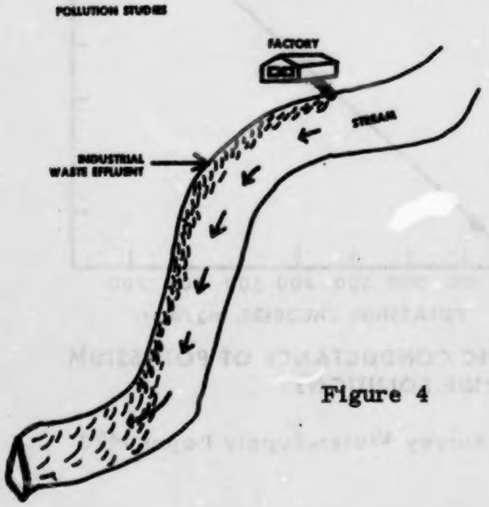

POLLUTION STUDIES
FACTORY
STREAM
INDUSTRIAL WASTE EFFLUENT

Figure 4

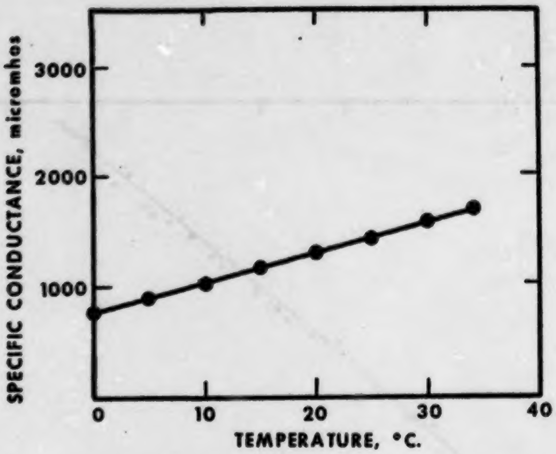


Figure 5. SPECIFIC CONDUCTANCE OF A 0.01 NORMAL SOLUTION OF POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES.

Geological Survey Water-Supply Paper 1473.

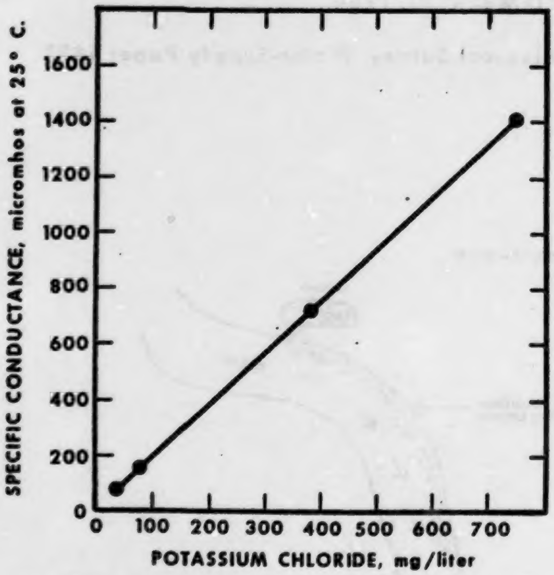


Figure 6. SPECIFIC CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS.

Geological Survey Water-Supply Paper 1473

VIII NPDES METHODOLOGY

A The Federal Register "List of Approved Test Procedures" for NPDES requirements specifies that specific conductance be measured with a self-contained conductivity meter, Wheatstone bridge type.(1) (2) (3)

Temperature directly affects specific conductance values (see Fig. 5). For this reason, samples should preferably be analyzed at 25°C. If not, temperature corrections should be made and results reported as μmhos/cm at 25°C.

1 The instrument should be standardized using KCl solutions. (See Fig. 6)

2 It is essential to keep the conductivity cell clean.

B The EPA manual specifies using the procedure as described in Standard Methods(2) or in ASTM Standards(3). These are approved in 40 CFR136 for NPDES Report purposes.

C Precision and Accuracy(1)

Forty-one analysts in 17 laboratories analyzed 6 synthetic water samples containing the following K_{sp} increments of inorganic salts: 100, 106, 808, 848, 1640 and 1710 micromhos/cm.

The standard deviation of the reported values was 7.55, 8.14, 66.1, 79.6, 106 and 119 μmhos/cm respectively.

The accuracy of the reported values was -2.0, -0.8, -29.3, -38.5, -87.9 and -86.9 μmhos/cm bias respectively.

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, EPA-AQCL, Cincinnati, Ohio 45268, 1974.

2 Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 14th Edition, 1976.

3 ASTM Annual Book of Standards, Part 31, 1975.

This outline was prepared by John R. Tilstra, Chemist, National Eutrophication Research Program, Corvallis, Oregon with additions by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Chemical Analysis, Concentration, Conductivity, Dissolved Solids, Electrical Conductance, Ions, Physical Properties, Salinity, Sodium, Specific Conductivity, Sulfates, Water Analysis, Water Supplies.

LABORATORY PROCEDURE FOR ACIDITY

I SCOPE AND APPLICATION

A Applicable to surface waters, sewages and industrial wastes, particularly mine drainage and receiving streams and other waters containing ferrous iron or other polyvalent cations in the reduced state.

B Range for a 50ml sample:
10 to 1000 mg acidity/liter

II APPARATUS

A A calibrated pH meter and electrode(s)

B Hot plate

C Magnetic stirring apparatus

III REAGENTS

For a detailed discussion of reagent preparation, consult REFERENCE I.

A Hydrogen Peroxide, 30% solution

B Standard Sodium Hydroxide (0.02N)
(Final normality is determined by standardization with potassium biphthalate).

C Standard Sulfuric Acid (0.02N)
(Final normality is determined by standardization with sodium carbonate).

D Carbon Dioxide-Free Distilled Water

IV PROCEDURE$^{(2)}$

A Pipet 50ml of the sample into a 150 ml beaker.

B Measure the pH of the sample. If the pH is above 4.0 add standard sulfuric acid in 5.0 ml increments to lower the pH to 4.0 or less. Record the volume of acid added. If the initial pH of the sample is less than 4.0, the incremental addition of sulfuric acid is not required.

C Remove the electrode(s).

D Add 5 drops of hydrogen peroxide and 3 glass boiling beads.

E Heat the sample to boiling and continue boiling for 2 to 4 minutes. In some instances, the concentration of ferrous iron in a sample is such that an additional amount of hydrogen peroxide and a slightly longer boiling time may be required.

F Cool the sample to room temperature.

G Titrate with standard sodium hydroxide, using a pH meter and gentle stirring, to pH 8.2

H Record volume of standard alkali used in in the titration.

V CALCULATIONS

A Acidity, as mg/L $CaCO_3$ =

$$\frac{[(A \times B) - (C \times D)] \times 50,000}{\text{ml sample}}$$

where:

A = vol. of standard alkali used in titration

B = normality of standard alkali

C = volume of standard acid used to reduce pH to 4 or less

D = normality of standard acid

50 = equivalent weight of $CaCO_3$

1000 - converts ml to liters

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater, 14 ed., 1975, APHA - AWWA - WPCF, Washington, D. C., 20036, p. 276.

2 Methods for Chemical Analysis of Water and Wastes, 1974, EPA - MDQARL, Cincinnati, Ohio 45268, p. 1.

This outline was prepared by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Acids, Acidity, Analytical Techniques, Chemical Analysis, Laboratory Tests, Neutralization, Water Analysis

LABORATORY PROCEDURE FOR TOTAL ALKALINITY

I SCOPE AND APPLICATION

A Applicable to drinking, surface and saline waters, domestic and industrial wastes.

B Suitable for all concentration ranges; however appropriate aliquots should be used to avoid a titrant volume greater than 50 ml.

II APPARATUS

A A calibrated pH meter and electrode(s)

B Magnetic stirring apparatus

III REAGENTS

For detailed discussion of reagent preparation, consult method reference 3.

A Carbon Dioxide - Free Distilled Water

B Standard Sodium Carbonate Solution

C Sulfuric Acid or Hydrochloric Acid Titrant (0.02N) Final normality is determined by standardization with sodium carbonate .

IV STANDARDIZATION OF THE ACID TITRANT

A Set the temperature reading on the pH meter dial to match the temperature of the buffer and sample solutions.

B Standardize the pH meter against a reference buffer solution. Check against a second buffer solution.

C Weigh accurately 0.088 ± 0.001 g of the dried sodium carbonate and transfer it to a 500 ml conical flask.

D Add 50 ml of water and swirl to dissolve the carbonate.

E While stirring the solution (magnetic bar and stirrer), add the sulfuric or hydrochloric acid titrant from a 100 ml buret until a pH of 4.5 is attained.

F Calculate the normality of the acid titrant as follows:

$$A = \frac{B}{0.053 \times C}$$

A = normality of the acid titrant

B = g of sodium carbonate used

C = ml of acid consumed

0.053 = milliequivalent weight of Na_2CO_3

V PROCEDURE(1)

A Pipette 50 ml of the sample into a 150 ml beaker.

B Titrate with the acid titrant, using a pH meter and gentle stirring, to pH 4.5.

C Record volume of standard acid used in the titration.

VI CALCULATIONS

Total alkalinity as mg of $CaCO_3/L$

$$\frac{A \times N \times 50000}{B}$$

A = ml of standardized acid titrant

N = N of standardized acid titrant

B = ml of sample

50 = equivalent weight of $CaCO_3$

1000 - converts ml to liters

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, EPA-MDQARL, Cincinnati, Ohio 45268, 1974, p. 3.

2 Standard Methods for the Examination of Water and Wastewater, 14th ed. 1975, p.278.

3 Book of ASTM Standards Part 31, 1975, p. 111.

This outline was prepared by C. R. Feldmann, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Alkalis, Alkalinity, Analytical Techniques, Chemical Analysis, Laboratory Tests, Neutralization, Water Analysis

LABORATORY PROCEDURE FOR TOTAL HARDNESS

I REAGENTS

A Buffer Solution:

1 Dissolve 16.9 g of NH_4Cl in 143 ml of conc. NH_4OH.

2 Dissolve 1.179 g of analytical reagent grade disodium ethylenediamine tetra-acetic acid dihydrate($Na_2EDTA \cdot 2H_2O$) and 0.644 g of $MgCl_2 \cdot 6H_2O$ in 50 ml of distilled water.

3 Add the solution from (2) to the solution from (1) with mixing, and dilute to 250 ml with distilled water. Addition of small amounts of $Na_2EDTA \cdot 2H_2O$ or $MgCl_2 \cdot 6H_2O$ may be necessary to attain exact equivalence.

4 The buffer should be stored in a plastic or resistant glass container tightly stoppered to prevent CO_2 absorption and NH_3 loss. Discard the buffer when 1 or 2 ml added to the sample fails to produce a pH of 10.0 ± 0.1 at the end point of the titration.

B Inhibitor:

1 Most water samples do not require the use of an inhibitor. In the presence of certain interferring ions, however, an inhibitor may be needed to sharpen the endpoint color change. Several types of inhibitors may be prepared or purchased. See Standard Methods (1) for discussion and choices.

C Indicator:

1 Eriochrome Black-T dye (EBT) is useful for the determination. Other commercial grades or laboratory formulations of the dye are also satisfactory. See Standard Methods (1) for other commercial equivalents.

2 Prepare the indicator in dry powder form by grinding together 0.5 g of the dye and 100 g of NaCl.

D Standard Calcium Calcium Carbonate, $CaCO_3$:

Weigh 1.000 g of anhydrous, primary standard grade $CaCO_3$ and transfer it to a 500 ml Erlenmeyer flask. Add 1:1 HCl (equal volumes of conc. HCl and water) dropwise and with swirling of the flask until the $CaCO_3$ has dissolved. Bring the volume of liquid to about 200 ml with water, boil a few seconds to dispel CO_2, cool, and add a few drops of methyl red indicator. Adjust the color of the solution to an intermediate orange by the dropwise addition of 1:1 HCl or 1:4 NH_4OH (1 volume of conc. NH_4OH + 4 volumes of water). Transfer the solution quantitatively to a one liter volumetric flask and dilute to the mark with water. (1.0 ml = 1.0 mg$CaCO_3$)

E $Na_2EDTA \cdot 2H_2O$ (0.01 M):

Dissolve 3.723 g of the dry reagent grade $Na_2EDTA \cdot 2H_2O$ in distilled water and dilute to 1 liter. 1.0 ml of the 0.01 M solution = 1.0 mg of $CaCO_3$. Check the concentration of this solution by titration against the standard calcium carbonate solution as described in II below.

II STANDARDIZATION OF THE $Na_2EDTA \cdot 2H_2O$ (1)

A Pipet 25.0 ml of $CaCO_3$ standard into either a 125 ml Erlenmeyer flask (if a combination pH electrode is to be used) or a 150 ml beaker (if two electrodes are to be used).

B Add 25 ml distilled water so the volume of $CaCO_3$ is about 50 ml.

C Place the container on a stirring mechanism. The solution should be stirred continuously for the remaining steps of the titration.

D Add 1 to 2 ml of the buffer solution.

E Check the pH of the mixture and ensure that it is 10.0 ± 0.1 Add drops of buffer solution if necessary. (The pH meter should be calibrated for use at this pH before you do this step).

F Add approximately 0.2 g of the indicator. A measuring scoop can be used.

G Add the $Na_2EDTA \cdot 2H_2O$ slowly and with stirring until the color changes from a rose to a blue color. The color change is more easily seen if the titration is carried out in daylight, or under a daylight fluorescent lamp and against a white background. If the color change is not sharp, repeat the determination using the inhibitor. If the endpoint is still not sharp, prepare a fresh supply of indicator.

H The titration should take less than 5 minutes, measured from the time of buffer addition.

I In an analysis of this type it is advantageous to carry out a preliminary, rapid titration in order to determine approximately how much titrant will be required. This is accomplished by adding the $Na_2EDTA \cdot 2H_2O$ at a fast dropwise rate until the color change is observed.

III PROCEDURE (1)

Repeat steps II A through II I using sample in place of $CaCO_3$ standard. The amount of sample taken should require less than 15 ml of $Na_2EDTA \cdot 2H_2O$ titrant.

IV CALCULATION

A Standardization of the $Na_2EDTA \cdot 2H_2O$:

ml of $CaCO_3$ equal to 1.0 ml of the $Na_2EDTA \cdot 2H_2O$:

$$B = \frac{\text{ml of } CaCO_3}{\text{ml of } Na_2EDTA \cdot 2H_2O \text{ required for titration}}$$

B Total Hardness

$$\text{Hardness as mg } CaCO_3/L = \frac{A \times B \times 1000}{\text{ml of sample}}$$

A = ml of $Na_2EDTA \cdot 2H_2O$ for titration of sample

B = the value obtained above.

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater. 14th Edition, APHA-AWWA-WPCF, 1975.

2 ASTM Standards, Part 31, Water; 1975.

3 Methods for Chemical Analysis of Water and Wastes, 1974, Environmental Protection Agency, EMSL, Cincinnati, Ohio.

This outline was prepared by C. R. Feldmann, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Calcium, Calcium Carbonate, Chemical Analysis, Hardness, Laboratory Tests, Magnesium, Water Analysis, Calcium Compounds, Analytical Techniques

AMPEROMETRIC DETERMINATION OF TOTAL RESIDUAL CHLORINE (BACK TITRATION FOR WASTEWATER SAMPLES)

I SCOPE AND APPLICATION

A This method is for the determination of total chlorine residual in domestic wastewater samples.

B It is applicable for concentrations of 1 to 10 mg Cl/liter. This range can be extended by dilution of the sample.

II APPARATUS

A End-point detection apparatus consisting of a cell unit connected to a microammeter, with the necessary electrical accessories.

1 Metal electrodes must be cleaned occasionally with a suitable abrasive.

2 The salt bridge must not be plugged with deposits.

3 Some undissolved salt should be in the reference electrode solution to ensure constant (saturated) composition. Fill the chamber about 2/3 full and add enough water to generously cover the tablets. Then plug the cell unit into the titrator and allow to stand for 24 hours immersed in about 200 ml of water or sample (contained in a sample cup) to establish equilibrium of the reference electrode.

4 When most of the tablets are used up, wash out the cell, clean the metal electrodes and refill the chamber as above.

5 When not in use, either store the cell immersed in 200 ml water or sample solution, or else remove all electrolyte and store it dry.

B Agitator

This part of the apparatus provides rapid and thorough mixing of the titrant and test materials, and also produces a continuous flow of the mixture past the electrode.

C Sensitizing Electrode and Agitator

The apparatus can lose its sensitivity to iodine. In this case, the pointer will not come on scale even when the adjusting knob is turned completely clockwise. Use the following steps to restore sensitivity.

1 Put about 150 ml of water containing 1 to 2 mg/liter available residual chlorine into sample cup. (Iodine solution diluted to a yellowish color can also be used. In this case, omit steps 3 and 4).

2 Place the cup on the assembly, immersing the electrodes and agitator.

3 Add potassium iodide crystals to the same water.

4 Add 1 ml acetate buffer solution, pH 4.0.

5 Turn on the agitator for about 3 minutes.

6 Then allow the electrodes and agitator to remain immersed for about 15 minutes.

7 Rinse them thoroughly with chlorine-demand-free water or the sample to be tested.

D Conditioning the Sample Cup

1 Fill glass sample cups with water containing at least 10 mg/liter residual chlorine.

2 Let stand for three hours or more.

3 Rinse thoroughly with chlorine-demand-free water.

III REAGENTS

A 0.0282 N Iodine Titrant

This solution can be purchased, but its concentration should be checked and, if necessary, adjusted to 0.0282 N. (Otherwise, change the calculation formula).

To prepare it, consult reference 1 for details of the following:

1 Prepare 0.1N arsinite solution. This solution is very TOXIC. Avoid ingestion.

2 Prepare 0.1N iodine solution, standardizing it with 0.1N arsenite solution.

3 Prepare 0.0282N iodine titrant by diluting the correct amount of 0.1N iodine solution. Store it in amber bottles or in the dark, and protect it from direct sunlight at all times. Avoid its contact with rubber. Even with precautions this solution needs a normality check with 0.1N arsenite solution each day of use. See reference 1 for details.

4 NOTE: 0.0282N Iodine has two uses. It is used to standardize phenylarsine oxide solution and it is used as a titrant in tests conducted with either phenylarsine oxide or sodium thiosulfate solutions. If sodium thiosulfate solution is to be used in the test, an alternative titrant is 0.00564N iodate solution. It is made with primary standard grade potassium iodate. Reference 1 has preparation details.

  a If you choose to use iodate titrant, prepare 100 ml 10% phosphoric acid solution.

B Starch Indicator Solution

This solution is used to standardize phenylarsine oxide solution. It is also used for tests conducted with iodate titrant.

See reference 1 for preparation details.

C 0.00564N Phenylarsine Oxide (PAO) Solution

1 ml = 1 mg/L available chlorine in a 200 ml sample. This solution can be purchased, but its concentration should be checked and, if necessary, adjusted to 0.00564N. (Otherwise, change the calculation formula). To prepare it, consult reference 1 for details of the following:

1 Prepare approximately 0.00564N PAO solution.

2 Adjust to final normality using results of titrating 0.0282N iodine titrant (starch indicator).

3 This PAO solution is very stable. It is also very TOXIC. Avoid ingestion.

4 NOTE: Alternatively, reference 1 has details for preparing and standardizing 0.1N sodium thiosulfate solution, aging it, then diluting it to a 0.00564N solution. This solution is unstable. It requires preservatives and daily standardization.

D Potassium Iodide Crystals or solution of 5 parts potassium iodide in 95 parts distilled water.

E Acetate Buffer Solution, pH 4.0

This solution can be purchased.

Consult reference 1 for preparation details.

IV PROCEDURE[2]

These steps utilize 0.00564N phenylarsine oxide and 0.0282N iodine titrant.

A Titrator

1 Plug the titrator into a source of 110 volt, single phase, 60 cycle ac power.

2 Check that the cell contains saturated electrolyte solution according to IIA3 above.

3 If necessary, sensitize the electrodes and agitator according to IIC above.

4 If necessary, condition the sample cup according to IID above.

5 If applicable to the apparatus, add phenylarsine oxide solution to the titrant reservior, screw it onto the reagent pump unit, and insert a 5 or 10 ml pipet in the assembly. Fill the pipet with PAO beyond the zero mark, then drain to the zero mark. This fills the delivery tube to the sample cup.

B Preparation of Test Mixture

1 If the sample cup is in place on the titrator, remove it. Empty any contents and thoroughly rinse it and the cell unit.

2 Measure 200 ml of the sample and carefully pour it into the cup.

3 Place the cup on the titrator with the top edge behind the cup guide post and with the bottom resting on the support provided. The tip of the plastic tubing to dispense the titrant should be in the cup.

4 Turn the switch on to start the agitator.

5 Pipet 5.0 ml 0.00564N phenylarsine oxide (PAO) solution into the sample. (If 5-10 mg Cl/liter is involved, add 10.0 ml of the PAO).

6 Add pH4 acetate buffer solution to reduce pH to 3.5-4.2. Usually 4ml is sufficient.

7 Add about 1 gram potassium iodide crystals or an eyedropper full of potassium iodide solution.

C Titration

1 Rotate the adjusting knob so that the microammeter pointer reads about 20 on the scale. (The reason is to have a reference point).

2 Use a 1 ml pipet or a buret (with offset tip), graduated in tenths or hundredths, to add 0.0282N iodine titrant in small increments. (Note: Do not use the pipetting apparatus incorporated in the instrument. Plastic components may react with the iodine solution and change its strength).

During the addition of iodine, the pointer will remain practically stationary until the end point is near. At that time, each dropwise addition of iodine causes a temporary deflection to the right, then the pointer returns to the original position.

When a drop of iodine causes a permanent deflection of the pointer to the right, you have reached the end point.

3 Record the volume of iodine solution used to reach the end point.

4 Unless the sample contains alum, leave it in the cup to keep the electrode assembly in readiness for other tests. If alum is present, use distilled water to rinse the cell unit two or three times. Fill the sample cup with distilled water and place it on the titrator to store the cell unit.

V CALCULATIONS

A Formula:

$$\text{mg/L Cl} = \frac{(A-5B)\times 200}{C}$$

A = ml 0.00564N phenylarsine oxide solution
B = ml 0.0282N iodine titrant
C = ml sample

References

1 Standard Methods for the Examination of Water and Wastewater, 14th edition, 1975, APHA-AWWA-WPCF, 1015 18th Street, N. W., Washington, D.C., 20036. p. 318.

2 Instruction Manual, Amperometric Titrator, Wallace and Tiernan, Belleville, New Jersey 07109.

This outline was prepared by Audrey D. Kroner, Chemist, National Training and Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268

Descriptors: Analytical Techniques, Chemical Analysis, Chlorine, Laboratory Tests, Water Analysis

USE OF A SPECTROPHOTOMETER

I SCOPE AND APPLICATION

A Colorimetry

Many water quality tests depend on a treating a series of calibration standard solutions which contain known concentrations of a constituent of interest, and also the sample(s) with reagents to produce a colored solution. The greater the concentration of the constituent, the more intense will be the resulting color. A spectrophotometer is used to measure the amount of light of appropriate wavelength which is absorbed by equal "thicknesses" of the solutions. Results from the standards are used to construct a calibration (standard) curve. Then the absorbance value for the sample is located on the curve to determine the corresponding concentration.

B Lambert Beer Law

States the applicable relationships:

$$A = e\ b\ c$$

1 A = absorbance

2 e = molar absorptivity

3 b = light path in cm

4 c = concentration in moles/liter

II APPARATUS

A Requirements

Are given as part of the method write-up

1 The applicable wavelength is specified. The unit used is nanometers (nm).

2 The light path (cell dimension) is often open-ended, e.g., "one cm or longer." One must know the light path length in the available spectrophotometer, because it is inversely related to the usable concentrations in the test. (Longer path lengths detect lower concentrations).

3 NOTE: For National Pollutant Discharge Elimination System (permit), or for Drinking Water Regulations test requirements, check with the issuing/report agency before using light paths (cells) that differ from the length specified in the approved method. If you have permission to use an alternate path length, concentrations for the test can be adjusted accordingly. These adjustments are discussed in IV and in VII (below).

III PREPARATION OF THE SPECTROPHOTOMETER

A Phototube/Filter

1 May have to choose a phototube for use above or below a particular wavelength.

2 A filter may be required.

3 If the available instrument involves a choice, check that the phototube (and filter, if applicable,) required for the wavelength to be used is in the instrument.

4 Always handle and wipe off the phototube and/or filter with tissue to avoid leaving fingerprints.

B Cell compartment

1 This area must be kept clean and dry at all times.

C Cells

1 A set must "match" each other in optical properties. To check this, use the same solution at the same wavelength, and verify that the absorbance value is the same for each cell.

2 Alternatively, a single cell can be used if it is thoroughly rinsed after each reading.

3 Instrument cells should be free of scratches and scrupulously clean.

- a Use detergents, organic solvents or 1:1 nitric acid-water.
- b Caustic cleaning compounds might etch the cells.
- c Dichromate solutions are not recommended because of adsorption possibilities.
- d Rinse with tap, then distilled water.
- e A final rinsing and drying with alcohol or acetone before storage is a preferred practice.

D Warm-Up

1 Plug in the power cord.

2 Turn the power switch on and give it an additional half-turn to keep the needle from "pegging."

3 Wait to use until the recommended warm-up time has passed. Anywhere from 10 to 30 minutes may be required.

4 If the instrument drifts during zeroing, allow a longer time.

E Wavelength Alignment

One reference is the known, maximum absorption for a dilute solution of potassium permanganate which has a dual peak at 526 nm and 546 nm. Use 2 matched cells for the following steps:

1 Prepare a dilute solution of potassium permanganate (about 10 mg/L).

2 Follow the steps in VI A, Zeroing Operation, using a wavelength of 510 nm, and distilled water as a "reagent blank." Keep the water in the cell during this entire procedure.

3 Rinse the matched cell two times with tap water, then two times with the permanganate solution.

4 Fill the cell three-fourths full with the permanganate solution. Keep the permanganate solution in this cell during this entire procedure.

5 Thoroughly wipe the cell with a tissue. Hold the cell by the top edges.

6 Open the cover and gently insert the cell, aligning it to the ridge as before.

7 Close the cover.

8 Record the wavelength and the absorbance reading on a sheet of paper.

9 Remove the cell of permanganate solution and close the cover.

10 Set the wavelength control at the next graduation (+ 5nm).

11 If the needle is not at infinite (symbol ∞) absorbance, use the left knob to re-set it.

12 Insert the cell containing distilled water using the techniques noted in 5, 6 and 7 above.

13 If necessary, use the right knob to re-set the needle at zero absorbance.

14 Remove the cell and insert the cell of permanganate solution using the techniques noted in 5, 6 and 7 above.

15 Record the wavelength and the absorbance reading.

16 Repeat steps 9 through 15 above until absorbance readings are recorded at 5 nm increments from 510 nm through 560 nm.

17 Make a graph plotting absorbance readings against wavelengths. With very good resolution, there will be two peaks - one at 525 nm and one at 545 nm. A single flat topped "peak" between these two wavelengths is acceptable.

18 If the maximum absorbances[peak(s)] occur below or above 526 nm or 546 nm, and at a number of scale units different from the stated instrument accuracy, the wavelength control is misaligned. To compensate for this until the instrument can be serviced, add or subtract the error scale units when setting wavelengths for subsequent tests.

IV CALIBRATION STANDARDS

A Requirements

A set of calibration standards is required, with concentrations usable in the available spectrophotometer cell (light path length).

1 The method reference may provide a table of light path lengths and the corresponding applicable concentration range for calibration standards, so one can choose the range required for his instrument cell or sample concentration.

2 The method reference may give directions for preparing one range of concentrations for a given light path length. If your cell provides a different length, your concentration requirements can be easily calculated by recalling that the light path length is inversely related to concentration. Thus, if your cell is twice the given path length, you need the given concentrations divided by two.

3 The method reference may give directions for preparing only one range of concentrations for the calibration standards, and then not be specific about the associated path length. You will have to test if the range is applicable to your instrument by preparing the given concentrations, obtaining absorbance values for them and checking the results according to section VII (below).

B Preparation

The calibration standards required for spectrophotometric measurements are so dilute, that they are commonly prepared by diluting stronger solutions. These are described in general terms below. Weights and volumes involved in preparing these solutions for a specific test can be found in the method write-up.

1 Stock Solutions

a Prepare by weighing or measuring a small amount of a chemical containing the constituent of interest and dissolving it to a one liter volume.

b Common stock solutions have concentrations in the range of 0.1 to 1.0 mg/ml.

c Most are refrigerated for storage and some are further treated by adding a preservative. Many are stable up to six months.

2 Standard Solutions

a Prepare by diluting a stock solution (at room temperature). Common volumes are 10.0 or 20.0 ml of stock diluted to one liter.

b Resulting standard solutions have concentrations in the range of 1.0 to 10.0 ug/ml.

c Although some standard solutions may be stable for a period of time, it is a recommended practice to prepare them on the day of use.

3 Calibration (Working) Standard Solutions

a Prepare by diluting a standard solution. Usually a set of calibration standards is required so that resulting concentrations give five to seven results within the sensitivity limits of the instrument. Common volumes are 1 to 10 ml of standard solution diluted to 100 ml.

b Resulting solutions might have concentrations in the range of 0.01 and 1.0 ug/ml.

c A reagent blank (distilled water) should be included in the set of standards.

4 Adjusting Concentrations

a You may find it necessary to adjust preparation quantities given in the method write-up, because your cell (light path length) differs from the example.

b These adjustments are discussed in A Requirements (above), and are usually applied to the Standard (intermediate) Solution.

C Chemical Treatment

1 Most colorimetric methods require that the calibration standards (including the reagent blank) are to be treated as the sample. Thus, they are to be processed through pretreatments and through the test as if they were samples. Then any test effects on sample results will be compensated by the same effects on results obtained for the treated standards.

2 One should be aware that pH is a critical condition for most colorimetric reactions. Ordinarily, a pH adjustment is included in the test method and reagents include chemicals to control pH. Thus,the processed standards correspond to the samples regarding pH, and thus they correspond in degree of color development. If standards are processed in some other manner, they must be pH adjusted to correspond to the samples at the time of color development.

V SAMPLE DILUTIONS

A Concentration Limits

The concentration of the sample must result in an absorbance within the range of the calibration standards, i.e., accurately detectable in the light path provided by the instrument. A dilution before analysis may be required to accomplish this. It is not accurate to dilute a sample after processing in order to obtain a usable absorbance reading.

1 Record dilution volumes so a dilution factor can be calculated and applied to results.

2 An analyst often has a good estimate of the expected concentration of a sample if s/he routinely tests samples from the same source. In this case, a single dilution, if any, is usually sufficient.

3 If a sample is from an unknown source, the analyst has several choices.

a Process the sample. If the reading shows it is too concentrated, dilute it until you get a value in the usable range. This result is not accurate enough to report, but you now know how to dilute the sample to process it through the test to get usable results.

b Prepare at least a 50% dilution and analyze it plus an undiluted aliquot.

c Prepare a variety of dilutions.

d Use some other analytical method to get a rough estimate of the expected concentration.

B Final Volumes

1 Dilute to a final volume sufficient to rinse the measuring glassware and provide the test volume cited in the referenced method.

2 Save any undiluted sample.

VI PROCEDURE FOR USING A SPECTROPHOTOMETER

A Zeroing Operation

The following steps have been written for spectrophotometers used in this course. Check the manual for the available instrument for the steps applicable for your work.

1 Set the wavelength control to the setting specified for the standards you are testing. Approach the setting by beginning below the number and dialing up to it.

2 If a cell is in the holder, remove it.

3 Close the cell holder cover.

4 Turn the power switch/zero control (left) knob until the needle reads infinite (symbol ∞) absorbance (on the lower scale).

5 Rinse a cell two times with tap water, two times with distilled water, then two times with the reagent blank solution.

6 Fill the cell about three-fourths full with reagent blank solution.

7 Thoroughly wipe the outside of the cell with a tissue to remove fingerprints and any spilled solution. Hold the cell by the top edges.

8 Open the cell holder cover and gently slide the cell down into the sample holder.

9 Slowly rotate the cell until the white vertical line on the cell is in line with the ridge on the edge of the sample holder.

10 Close the cover and turn the light control (right) knob until the needle reads zero absorbance (on the lower scale).

11 Record an absorbance of zero for this zero concentration solution on a data sheet. (See next page).

12 Slowly remove the cell and close the cover. (No solution should spill inside the instrument). Keep the solution in the cell.

13 The needle should return to the infinite absorbance setting. It it does not:

a Reset the needle to the ∞ absorbance mark using the power switch/zero (left) control knob.

b Re-test the reagent blank solution using steps 7 through 12 above.

c If the needle does not return to the ∞ absorbance mark, another setting as noted in a. and b. is required. Additional warm-up time may be necessary before these settings can be made.

B Reading Absorbances

Using a single cell in the spectrophotometers used in this course

1 Discard any solution in the cell.

2 Rinse the cell two times with tap water, and two times with distilled water. Then rinse it two times with the lowest concentration standard remaining to be tested, or with processed sample.

3 Fill the cell about three-fourths full with the same standard or sample.

4 Use a tissue to remove any fingerprints from the cell and any droplets on the outside. Hold the cell by the top edges.

5 Open the cell holder cover and gently slide the cell down into the sample holder.

6 Slowly rotate the cell until the white vertical line on the cell is in line with the ridge on the edge of the sample holder.

7 Close the cover.

8 Record the concentration of the standard and its absorbance on a data sheet. (For a sample, record its identification code and its absorbance on the data sheet).

DATA SHEET	
Concentration mg/liter	Absorbance
0.00	
SAMPLE	
SAMPLE	

9 Repeat steps 1 through 8 (above) for each standard and sample to be tested. If a large number of measurements are to be made, check the instrument calibration every fifth reading.

a Use another aliquot of a solution already tested to see if the same reading is obtained. If not, repeat the zeroing operation in A (above).

b Alternatively, you can use the blank, if supply permits, and repeat the zeroing operation in A. (above).

10 When all the readings have been obtained, discard any solution remaining in the cell and rinse the cell with tap water. Clean the cell more thoroughly, (III C. 3), as soon as possible.

11 If no other tests are to be done, turn off the instrument, pull out the plug and replace any protective covering.

VII CHECKING RESULTS

A Readings Greater Than 0.70

On our instrument, these are considered to be inaccurate. Check the manual for your instrument or check the scale divisions to determine the limit for other models.

1 Do not use readings greater than 0.70 to develop a calibration curve.

2 From five to eight points (counting zero) are recommended for constructing a calibration curve. If you have fewer than five usable values, you should not draw a curve.

3 To prevent excessively high values in future tests, decrease the cell path length, if possible, by using an adapter and smaller cell.

4 If you cannot decrease the cell path length, you can at least obtain enough values to construct a curve. Prepare standards with five to eight concentrations ranging from zero to the concentration of the standard having an absorbance nearest to 0.70. This gives you more values for a curve, but it reduces the applicable range of the test. Usually the sample can be diluted before testing so the result will fit on the standard curve.

B Highest Reading is Less Than 0.6

1 Increase the cell path length by using a larger cell. A higher reading results.

2 Prepare a different set of standards with greater concentrations.

VIII CONSTRUCTING A CALIBRATION CURVE

If you have from five to eight usable absorbance values, you can construct a concentration curve.

A Graph Paper

Should be divided into squares of equal size in both directions

B Concentration Axis

1 Labeling

The longer side should be labeled at equal intervals with the concentrations of the calibration standards marked from 0.0 to at least the highest concentration recorded for the standards on the data sheet.

2 Units

a It is most convenient to express these concentrations in the units to be reported. Otherwise, a unit-conversion factor would have to be applied to obtain final, reportable values every time you use the curve.

b Example: If you dilute a standard solution to make 100.0 ml volumes of calibration standards, you have a choice in expressing the resulting concentrations. You can use weight/100 ml, or you can calculate weight/1 liter. If you are to report results as weight/liter, but you construct your curve using weight/100 ml, you will have to multiply every sample result from the curve by $\frac{1000}{100}$ or 10 to obtain the reportable value. It is much easier to convert the original calibration standard concentrations to the desired units and to use these as labels on the graph.

C Absorbance Axis

1 Labeling

The shorter side should be labeled at equal intervals with absorbance numbers marked from 0.00 to at least 0.70 absorbance units.

D Plotting the Curve

1 Use the absorbances recorded for each standard concentration to plot points for the curve.

2 The points should fall in a reasonably straight line.

3 Use a straight-edge to draw a line of best fit through the points. If the points do not all fall on the line, an acceptable result is an equal number of points falling closely above, as well as below the line. Experience provides a basis for judging acceptability.

4 It is not permissable to extrapolate the curve.

IX USING THE CALIBRATION CURVE

A Finding concentration of the sample

1 Use the absorbance value(s) recorded for the sample(s), and the calibration curve to find the concentration(s). If the concentration units differ from those required for reporting results, apply a unit conversion factor (VIIIB. 2).

2 If more than one dilution of a sample was tested, use the result that falls nearest the middle of the curve.

B If a sample was diluted, calculate the dilution factor and apply it to the concentration you find for the sample from the calibration curve.

1 Dilution Factor=

$$\frac{\text{final dilution volume}}{\text{ml sample used in dilution}}$$

2 Example: You diluted 10 ml sample to 50 ml. The concentration found by using a calibration curve was 0.5 mg/liter.

Then·

$$\text{constituent, mg/l} = \frac{50\text{ml}}{10\text{ ml}} \times \frac{0.5\text{ mg}}{\text{liter}}$$

$$= 2.5\text{ mg/liter}$$

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Descriptors: Analytical Techniques, Chemical Analysis, Colorimetry, Laboratory Tests, Spectrophotometry

LABORATORY PROCEDURE FOR TOTAL PHOSPHORUS

I SCOPE AND APPLICATION

A This method is for the determination of total phosphorus in drinking, surface and saline waters and in domestic and industrial wastes.

B It is applicable for concentrations of 0.01 to 1.0 mg P/liter. This range can be extended by dilution of the sample.

II APPARATUS

A Spectrophotometer with a light path of 1 cm or longer for measurements at 650 or 880 nm

B pH meter and electrode(s) to fit 125 ml Erlenmeyer flask

C Filtration assemblies for 0.45 μm discs, to filter about 10 ml test solution

III PREPARATION OF GLASSWARE (1)

A Traces of phosphorus on the glassware used in the test will cause significant errors. The glassware and filtration apparatus should be acid-washed. If this equipment can be reserved to use only for this test, the acid wash is only required occasionally.

1 Wash equipment with hot 1:1 HCl in a hood. Wear rubber gloves.

2 Rinse with tap water, then distilled water.

3 Fill or rinse each piece with the combined reagent used in the test to check for traces of phosphorus. A blue color will form if phosphorus is present.

4 Repeat the washing instructions until all phosphorus is removed (no color).

5 Then rinse everything several times with distilled water and allow it to dry.

IV PREPARATION OF FILTER DISCS

The 0.45 μm filter discs must be phosphorus-free. These can be purchased or you can treat discs as follows:(2)

A Soak the discs in distilled water, about 2 liters for every 50 discs, for 1 hour.

B Pour off the water and replace it.

C Soak the discs another 3 hours.

D Pour off water and dry.

E Check two or three dried discs by placing them in a small volume of combined reagent. If a blue color develops, phosphorus is present and you should repeat the wash operations. If no color develops, the discs are ready for use.

V REAGENTS(1)

A 10N Sodium Hydroxide

Dissolve 40 grams sodium hydroxide in about 80 ml distilled water. Caution: heat and fumes are liberated. Cool and dilute to 100 ml.

B 0.1N Sodium Hydroxide

Dilute 1 ml 10N sodium hydroxide to 100 ml.

C 11N Sulfuric Acid

Slowly add 310 ml conc. sulfuric acid to 600 ml distilled water. When cool, dilute to one liter.

D 0.11N Sulfuric Acid

Dilute 1 ml 11N sulfuric acid to 100 ml.

E 5N Sulfuric Acid

Slowly add 70 ml conc. sulfuric acid to 400 ml distilled water. Caution: Heat is liberated. When cool, dilute to 500 ml.

F Antimony Potassium Tartrate Solution

Weigh 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2\ H_2O$. Dissolve in 400 ml distilled water in a 500 ml volumetric flask and dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

G Ammonium Molybdate Solution

Dissolve 20 g$(NH_4)_6Mo_7O_{24} \cdot 4H_20$ in 500 ml of distilled water. Store in a plastic bottle at 4°C.

H 0.1M Ascorbic Acid

Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

I Combined Reagent

This reagent must be freshly prepared for each run. For 100 ml, mix E. F. G. and H. in the following proportions and order. (All reagents must be at room temperature)

1 50 ml 5N sulfuric acid.

2 5 ml antimony potassium tartrate solution. Mix well. If turbidity forms, let mix stand a few minutes, then shake again. Repeat until turbidity disappears.

3 15 ml ammonium molybdate solution. Mix well. Follow directions in 2. if turbidity forms.

4 30 ml 0.1M ascorbic acid. Mix well. Follow directions in 2. if turbidity forms.

J Ammonium Persulfate

No preparation is required. This is a vigorous oxidizing agent so store it with appropriate caution.

K Stock Phosphorus Solution

Weigh 0.2197 grams of potassium dihydrogen phosphate, KH_2PO_4, which has been dried at 105°C and cooled. Dilute to 1 liter in a volumetric flask. This solution is stable up to 6 months if stored at 4°C.

1.0 ml= 0.05 mgP.

L Standard Phosphorus Solution

1 This solution should be prepared at the time of use. It is for tests utilizing 1 cm spectrophotometer cells. For other light path lengths, adjust the concentration accordingly.

2 Dilute 20.0 ml stock phosphorus solution (at room temperature) to 1 liter in a volumetric flask.

3 1.0 ml= 1.0μgP.

VI PROCEDURE(1)

A Preparation of Calibration Standards

1 Mark nine 50 ml volumetric flasks with the concentrations listed in Table 1.

2 Using volumetric pipets, measure the amounts of standard phosphorus solution listed in the table into the corresponding 50 ml flask.

TABLE 1

Use These mls St'd P sol/50 ml	For this Conc., mg P/liter	Absorbances
0	0.00	
1.0	0.02	
3.0	0.06	
5.0	0.10	
10.0	0.20	
20.0	0.40	
30.0	0.60	
40.0	0.80	
50.0	1.00	
SAMPLE		

3 Dilute each to the 50.0 ml mark, stopper and mix thoroughly.

4 Note: The flask containing 50 ml distilled water (0.00 mgP) is the reagent blank.

5 Mark nine 125 ml Erlenmeyer flasks with the concentrations listed in Table 1.

6 Pour the nine standards into the corresponding Erlenmeyer flask.

B Measurement of Sample

1 Label a 125 ml Erlenmeyer flask with the sample identification code.

2 Shake the sample.

3 Immediately pipet 50 ml of sample into the flask.

a If the P concentration of the sample is unknown or if it is known to be greater than 1.0 mg/l, use the well shaken sample to make appropriate dilutions in 50 ml volumetric flasks.

b Record the ml of sample used in dilution.

c Transfer the 50 ml dilution(s) to 125 ml Erlenmeyer flasks that have been labeled with the ml of sample used in the dilution.

C Digestion of Calibration Standards and Sample(s)

1 Turn on the hot plate(s). You need surface area for all the 125 ml Erlenmeyers flasks containing standards and sample.

2 Use a 10 ml graduated pipet to add 1 ml 11N sulfuric acid to each flask.

3 Use a measuring scoop to add 0.4 gram ammonium persulfate to each flask.

4 Add 4 glass boiling beads to each flask.

5 Swirl each flask to thoroughly mix the contents.

6 Place the flasks on a hot plate and gently boil for 30-40 minutes or until a volume of about 10 ml is reached. CAUTION: Do not allow any to go to dryness. Alternately, the flasks may be autoclaved for 30 minutes at 121°C (15-20 psi).

7 Cool the flasks. If necessary, add distilled water so the volume of each is about 30 ml.

D pH Adjustment of Standards and Sample(s)

1 Adjust the pH of each solution to 7± 0.2, using a pH meter as follows:

a CAUTION: Be sure any buffer solution used to calibrate the meter has been completely flushed off the electrode(s). Use combined reagent to check the electrode(s), then rinse with distilled water.

b Add 10N sodium hydroxide rapidly to a pH of 3, then dropwise to a pH of 6.

c Add 0.1N sodium hydroxide dropwise until the pH is between 6.8-7.2. If you over-shoot the desired pH, add 0.11N sulfuric acid dropwise until the pH is between 6.8-7.2.

d Rinse the electrode(s) with a very small quantity of distilled water, collecting the rinse in the flask of solution tested.

E Filtration of Standards and Sample(s)
If a sample is not clear at this point,

1 Add 2-3 drops of 11N sulfuric acid to the turbid sample(s).

2 Filter the solution through individual phosphorus-free, 0.45 µm pore size filter discs. Collect filtrate.

a Be sure filter apparatus is free of phosphorus contamination.

b Rinse each Erlenmeyer flask with two 5 ml portions of distilled water and filter each portion through the corresponding disc.

F **Volume Adjustment**

After D. pH adjustment and possibly E. Filtration, the standards and sample(s) are at volumes other than 50 ml. Accordingly:

1 Pour each solution back into the 50 ml volumetric flask used to prepare it. (You will need an additional 50 ml flask for any undiluted sample(s).

2 If there is less than about 45 ml in the volumetric flask, use about 4 ml distilled water to rinse the container into the 50 ml volumetric flask.

3 Dilute each solution to the 50.0 ml mark.

4 Stopper and invert each flask to thoroughly mix the contents.

5 Thoroughly rinse and shake dry the 125 ml Erlenmeyer flasks originally used for the solutions.

6 Return each solution to its corresponding (cleaned) 125 ml Erlenmeyer flask.

G **Colorimetry**

1 Pipet 8.0 ml of combined reagent into each Erlenmeyer flask.

2 Gently swirl each flask.

3 Note the time. After 10 minutes (and not more than 30 minutes), make spectrophotometric readings at 880 nm. (650 nm may also be used).

a Use the 0.00 mgP/liter reagent blank to calibrate the instrument.

b Record the absorbances in Table 1 (A 2 above) next to the corresponding concentrations of the standards. A space is also provided for recording the absorbance of the sample.

VII CALIBRATION CURVE

A Obtain a piece of graph paper and label the axes. The longer side should be labeled with the concentrations of the standards as given in Table 1. The shorter axis is labeled from 0.00 to 1.00 as the absorbance axis.

B Use the absorbances recorded for the standards in Table 1 and the corresponding concentration of the standards to plot a calibration curve.

VIII RESULTS

A Use the absorbance value recorded in Table 1 for the sample to find the total phosphorus concentration from the curve.

1 If more than one dilution was run, use the result that falls nearest the middle of the curve.

B **Dilution Factor**

If the sample was diluted, calculate the dilution factor and apply it to the concentration you found for the sample by using the curve.

1 Dilution Factor =

$$\frac{\text{50 ml}}{\text{ml sample used in dilution}}$$

2 Example: You diluted 10 ml sample to 50 ml. The concentration found using the curve was 0.4 mg/L. Then:

$$\text{Total P, mg/L} = \frac{\text{50 mL}}{\text{10 mL}} \times \text{0.4 mg/L}$$

$$\text{Total P, mg/L} = 2.0$$

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, 1979, U.S. EPA, EMSL, Cincinnati, OH, 45268.

2 Standard Methods for the Examination of Water and Wastewater, 14th edition, 1975, APHA-AWWA-WPCF, Washington, D.C., 20036.

This outline was prepared by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, MOTD, OWPO, USEPA, Cincinnati, Ohio 45268

Descriptors: Analytical Techniques, Chemical Analysis, Laboratory Tests, Nutrients, Phosphorus, Water Analysis

FLUORIDE ANALYTICAL PROCEDURES-SPADNS

I SPADNS PHOTOMETRIC METHOD

A Reagents

1 Acid - zirconyl - SPADNS reagent:

  a Dissolve 0.958 g. SPADNS in about 300 ml distilled water, contained in a 1 - liter volumetric flask.

  b Dissolve 0.133 g zirconyl chloride octahydrate in about 150 ml distilled water and add to the flask. Rinse the container and add the rinses to the flask.

  c Add 350 ml concentrated HCl to the flask, swirling to mix well.

  d Add distilled water to the liter mark.

  e The combined reagent is stable for at least two years.

2 Fluoride stock solution: 0.2210 g NaF dissolved in 1 liter distilled water (1 ml = 0.1 mg F).

3 Standard fluoride solution: dilute above stock solution 1:10 with distilled water (1 ml = 0.01 mg F), or dilute 1:100 to make 1.0 mg/L F standard.

4 Sodium arsenite solution: 5.0 g $NaAsO_2$ dissolved in 1 liter distilled water. (Used as necessary for removal of chlorine in samples).
CAUTION: TOXIC

B Procedure

1 Prepare two separate standards in 125 ml erlenmeyer flasks as follows:

  a 0 mg/L standard - carefully measure (with a volumetric pipet) 50 ml of distilled water.

  b 1.0 mg/L Standard - carefully measure (with a volumetric pipet) 50 ml of 1.0 mg/L F standard solution.

2 Carefully measure 50-ml portions of each unknown sample into labeled, 125 ml erlenmeyer flasks.

3 Pipet 10.00 ml of acid - zirconyl - SPADNS reagent into each flask containing a standard or sample

4 Carefully swirl each of the standards and sample(s) to mix them with reagent. The materials must be thoroughly mixed.

5 With the distilled-water standard (0 mg/L F) in the cuvette, adjust the photometer slit so that a reading of .300 or .500 on the absorbance scale is obtained. Use a wavelength of 570nm.

6 Replace the 0 mg/L standard with the other standard and samples in succession, noting the absorbance reading in each case. (There is no minimum color development time).

7 Calculate the fluoride content of the unknown samples by the formula:

$$X = \frac{A_o - A_x}{A_0 - A_1}$$

where X is the fluoride content of the sample in mg/L,

where A_o is the absorbance reading of the 0 mg/L standard,

where A_x is the absorbance reading of the unknown sample, and

where A_1 is the absorbance reading of the 1.0 mg/L standard.

If preferred, a curve may be drawn by plotting the absorbance readings of the two standards and connecting with a straight line. The line may be extended to 1.4 mg/L, but no further.

Reference

1 Standard Methods for the Examination of Water and Wastewater, 14th ed., 1976, APHA-AWWA-WPCF, Washington, D.C. p. 393.

This outline was prepared by Dr. E. Bellack, Office of Water Supply, EPA, Washington, D.C.

Descriptors: Analysis, Chemical Analysis, Fluoridation, Fluorides, Fluorine, Water Analysis.

FLUORIDE ANALYTICAL PROCEDURES - ELECTRODE

I ELECTRODE METHOD USING A pH METER(1)

A Reagents

1 TISAB

a Place approximately 500 ml distilled water in a 1 - liter beaker. Add 57 ml conc. acetic acid, 58 g. sodium chlorine and 4.0 g 1, 2 cyclohexylene diamine tetraacetic acid (CDTA)* Stir to dissolve.

b Place the beaker in water bath (for cooling), insert a calibrated pH electrode and a reference electrode into the solution and slowly add approximately 6N sodium hydroxide (about 125 ml with stirring) until the pH is between 5.0 and 5.5 Put into a 1-liter volumetric flask and add distilled water to the mark. Mix well.

2 Fluoride stock solution

a Dissolve 0.2210 g. sodium fluoride in 1 liter of distilled water (1 ml = 0.1 mg F).

3 Standard fluoride solution

a Dilute 20 ml of the above stock solution to 1 liter (1 ml = 0.002 mg F).

B Procedure

1 Prepare a series of standards by pipetting the indicated amounts of standard fluoride solution into labeled 150-ml beakers, adding the indicated amounts of distilled water (by pipet).

ml Standard Soln.	ml Dist. Water	mg F	mg/L F
5	45	0.01	0.2
10	40	0.02	0.4
15	35	0.03	0.6
20	30	0.04	0.8
25	25	0.05	1.0
50	0	0.10	2.0

2 Pipet 50.0 ml of each sample into a labeled 150 ml beaker.

3 Using a pipet, add 50.0 ml TISAB to each beaker of standard or sample.

4 Bring standards and samples to the same temperature (plus or minus 2°C), preferably room temperature.

5 Immerse the electrodes and measure the developed potential while stirring the test solutions with a magnetic stirrer. Allow the electrodes to remain in the solution for 3 minutes before taking a final mv reading. Rinse electrodes with distilled water and blot dry between use in each solution. Record mv reading for each standard and sample. Confirm the electrode calibration by checking the reading of the 1.0 mg/L standard between each standard and sample. Adjust the calibration control as necessary until the meter reads as before.

6 Plot the potential measurement of standards in mv along the arithmetic horizontal axis of 2-cycle semilogarithmic graph paper. Plot mg/L on the vertical logarithmic axis, starting with 0.1 mg/L at the bottom.

7 Read the fluoride concentration of the unknown samples from the standard curve prepared from the readings obtained on the standards.

OUTLINE CONTINUED ON
NEXT PAGE

* CDTA is also listed as 1, 2 cyclohexylene dinitrilo tetraacetic acid

II ELECTRODE METHOD USING SELECTIVE ION METER(2)

A Reagents

1 TISAB

a Prepare as for Electrode Method. See I.A.1. above.

2 Fluoride stock solution

a Prepare as for Electrode Method. See I.A.2 above.

3 Standard fluoride solutions

a Dilute fluoride stock solution 1:10 with distilled water to make 10.0 mg/L standard (1 ml = 0.01 mg F).

b Dilute fluoride stock solution 1:100 with distilled water to make 1.0 mg/L Standard (1 ml = 0.001 mg F).

B Procedure

1 Measure two standards:

a In a 150 ml beaker labeled "1.0 mg/L" add by pipet 50 ml of the 1.0 mg/L fluoride standard solution.

b In a 150 ml beaker labeled "10 mg/L" add by pipet 50 ml of the 10.0 mg/L fluoride standard solution.

2 Add 50 ml (by pipet) of TISAB to each of the standards. Stir or swirl to mix.

3 Pipet 50 ml of each sample into a labeled 150 ml beaker.

4 Add 50 ml (by pipet) of TISAB to each sample. Stir or swirl to mix.

5 Immerse the electrodes in the 1.0 mg/L standard. Set the selector of a Model 407A meter on "X^-". Stir or swirl the beaker gently for 3 minutes. On the Model 409 meter, the selector should be set at "0.5 - 2".

6 Adjust the meter so that the pointer reads 1.0 mg/L. Use the calibration knob on a Model 407A or the "0.5 - 2" knob on a Model 409.

7 Turn off the meter, lift the electrodes, rinse them in distilled water and pat dry with a tissue.

8 Immerse the electrodes in the 10 mg/L standard, set the selector of a Model 407A meter on "X^-" or that of a Model 409 on "0.1 - 10". Stir or swirl the beaker gently for 3 minutes. Adjust the meter until the pointer indicates 10.0 mg/L, using the Temperature Compensator on a Model 407A or the "0.1 - 10" knob on a Model 409. Turn off the meter, rinse and dry the electrodes after each use.

9 Immerse the electrodes in a sample, set the meter selector to "X^-" or "0.5 - 2". Stir or swirl the beaker gently for 3 minutes and read the fluoride concentration directly from the meter scale. If the fluoride concentration is 2 on the Model 409, set the selector at "0.1 - 10" to obtain the reading.

REFERENCES

1 Standard Methods for the Examination of Water and Wastewater, 14th ed., 1975, APHA-AWWA-WPCF. Washington, D.C. p. 391

2 Orion Research, Inc., Analytical Methods Guide. October 1971

This outline wast prepared by Dr. E. Bellack, Office of Water supply, EPA, Washington, D.C.

Descriptors: Analysis, Chemical Analysis, Fluoridation, Fluoride, Fluorine, Water Analysis.

DETERMINATION OF NITRATE/NITRITE NITROGEN (CADMIUM REDUCTION METHOD)

I SCOPE AND APPLICATION

A This method is for the determination of total nitrate and nitrite nitrogen in drinking, surface and saline waters, domestic and industrial wastes. By carrying out the procedure without the initial reduction step, the method determines only nitrite nitrogen. Thus separate nitrate nitrogen and nitrite nitrogen values can be obtained by carrying out the procedure first with, and then without, the initial reduction step.

B The applicable range of this method is 0.01 to 1.0 mg/liter nitrate/nitrite nitrogen. The range may be extended by dilution of the sample.

II APPARATUS

A Spectrophotometer with a light path of 1 cm or longer for measurements at 540 nm.

B pH meter and electrode(s).

C Reduction Column.

1 Cut off both ends of a 100 ml volumetric pipet so that it measures 10 cm from the base of the cup to the top, and about 25 cm from the base of the cup to the end of the column.

2 Use glass wool as a plug for the column.

3 Attach a piece of tygon tubing (about 7.5 cm length) to the lower end of the column.

4 Put two screw clamps around the tygon tubing. The upper clamp is used to adjust the flow rate and the lower is used to stop the flow of solution.

5 Put the clamp in a buret support on a ring stand.

6 You can purchase reduction columns for this procedure.

III REAGENTS(1)

A Distilled Water

An ion exchange column in conjunction with a still provides an adequate supply of highly pure water.

B Concentrated Ammonium Chloride - EDTA Solution

Dissolve 13g ammonium chloride and 1.7g disodium ethylenediamine tetraacetate in 900 ml distilled water. Adjust to pH 8.5 with concentrated ammonium hydroxide and dilute to 1 liter with distilled water.

C Dilute Ammonium Chloride - EDTA Solution

Dilute 300 ml concentrated ammonium chloride - EDTA Solution to 500 ml with distilled water.

D Color Reagent

Add 100 ml concentrated phosphoric acid to about 800 ml distilled water in a 1 liter volumetric flask. Mix well. Dissolve 10g sulfanilamide and 1g N(1-naphthyl)-ethylenediamine dihydrochloride in the acid mixture. Mix, then dilute to 1 liter with distilled water.

E Zinc Sulfate Solution (Turbidity Removal)

Dissolve 100g zinc sulfate heptahydrate in distilled water and dilute to 1 liter.

F 6$\underline{N}$ Sodium Hydroxide Solution (Turbidity Removal)

Dissolve 24g sodium hydroxide in about 80 ml distilled water. Caution: Heat and fumes are liberated. Swirl to dissolve and cool the mixture. Dilute to 100 ml with distilled water.

G Non-polar Solvent (Oil and Grease Removal), a supply of freon, chloroform or equivalent.

H conc. Ammonium Hydroxide (pH adjustment)

I conc. Hydrochloric Acid (pH adjustment)

J 6N Hydrochloric Acid

Add 50 ml conc. hydrochloric acid to about 45 ml distilled water. Swirl, cool and dilute to 100 ml.

K 2% Copper Sulfate Solution

Dissolve 20g copper sulfate pentahydrate in 500 ml distilled water. Dilute to 1 liter.

L Granulated Cadmium

Each column requires about 20g cadmium, granulated to pass a 10 mesh sieve and to be retained on a 40, then a 60 mesh sieve. Filing stick cadmium should be done in a hood to avoid inhalation of small particles. The correct mesh cadmium can be purchased.

M Stock Nitrate Solution

Weigh out 7.218g potassium nitrate, dissolve it in distilled water and dilute to 1 liter. Preserve with 2 ml chloroform. This solution is stable up to 6 months if stored at 4°C.

1.0 ml = 1.00 mg nitrate nitrogen

N Column-Activation Nitrate Solution

This solution should be prepared at the time of use. It is required only when the cadmium has been washed with acid and copperized to prepare or to re-activate a column.

1 Dilute 1.0 ml stock nitrate solution (at room temperature) to 1 liter in a volumetric flask.

2 1.0 ml = 0.001 mg nitrate nitrogen

O Standard Nitrate Solution

This solution should be prepared at the time of use. It is for tests utilizing 1 cm spectrophotometer cells. For other light path lengths, adjust the concentration accordingly.

1 Dilute 10.0 ml stock nitrate solution (at room temperature) to 1 liter in a volumetric flask.

2 1.0 ml = 0.01 mg nitrate nitrogen.

P Stock Nitrite Solution

Weigh out 6.072g potassium nitrite, dissolve it in distilled water and dilute to 1 liter. Preserve with 2 ml chloroform. The solution is stable up to 3 months if stored at 4°C.

1.0 ml = 1.00 mg nitrite nitrogen.

Q Standard Nitrite Solution

This solution should be prepared at the time of use. It is for tests utilizing 1 cm Spectrophotometer cells. For other light path lengths, adjust the concentration accordingly.

1 Dilute 10.0 ml stock nitrite solution (at room temperature) to 1 liter in a volumetric flask.

2 1.0 ml = 0.01 mg nitrite nitrogen

IV PREPARATION OF REDUCTION COLUMN(1)

A Copperizing the Cadmium

1 Weigh out about 20g cadmium granules and place them in a 400ml beaker.

2 Add enough 6N hydrochloric acid to cover the granules.

3 Swirl, then decant off the acid. (Note: All through this procedure, decant into a filter paper in a funnel supported in an old bottle, etc., whenever small particles of cadmium are part of the decanted material.)

4 Add enough distilled water to cover the granules.

5 Swirl to wash, then decant off the water.

6 Wash the granules two times more using steps 4 and 5 above. The color of the cadmium should be silver.

7 Pour about 100 ml 2% copper sulfate solution over the granules.

8 Swirl until the blue color of the copper sulfate fades (about 5 minutes). A brown, very fine precipitate of metallic copper should form.

9 Decant off the copper sulfate solution.

10 If no brown precipitate was observed in step 8, do another 2% copper sulfate treatment using steps 7-9 above.

11 Remove all the brown precipitate by adding at least 10 distilled water rinses (in about 75 ml amounts), and decanting off the precipitate into the filter paper set-up described in 3 above. Using a spatula to move the precipitate along with the water facilitates this operation.

12 The cadmium so treated should be black.

B Checking Granule Size

1 Use a spatula to transfer the copper-cadmium granules to a 60 mesh sieve.

2 Hold the sieve over the filter paper set-up. Squirt distilled water over the granules at least three times to wash any "fines" through the sieve.

3 Use the squeeze bottle for distilled water and a spatula to return the granules to the beaker.

4 Decant off excess water.

C Filling the Column

1 Close one of the clamps on the delivery tube of the column.

2 Slowly fill the column almost to the top of the cup with distilled water. Release any air pockets that are formed.

3 Slowly add the copper-cadmium granules and allow them to "float" down through the water. Use a spatula to move the wet granules out of the beaker. Continue this addition until you have loosely filled the column up to about 2 cm below the cup-like section. (The column of granules should be about 18.5 cm in length).

D Checking the Flow Rate

1 Place a graduate under the column and open the screw clamp.

2 Time the rate of flow. It should be between 7 ml and 10 ml/minute.

3 If the flow rate is too fast, tighten the screw clamp and re-check the rate. Do this until the flow is 7-10 ml/minute. If the clamp shuts off the flow before the desired rate is obtained, add more copper-cadmium granules to the column. Continue checking the rate and adding granules until the 7-10 ml/minute rate is achieved. DO NOT let the column go dry.

4 If the flow rate is too slow, loosen the clamp and re-check the rate. If the 7-10 ml/minute rate cannot be achieved, remove some of the granules through the cup end of the column and re-check the rate. DO NOT let the column go dry.

5 When the 7-10 ml/minute flow rate is achieved, allow the remaining solution to drain until it is about 2.5 cm above the top of the granules. Use the second clamp to stop the flow of solution from the column.

6 Wash the column with a total of 200 ml dilute ammonium chloride - EDTA solution.

7 Allow this to drain through at the established flow rate of 7-10 ml/minute. Stop the flow when the solution is about 2.5 cm above the top of the granules.

8 The column of granules should always be covered with solution. When the column is not is use, use distilled water or dilute ammonium chloride - EDTA solution to cover the granules. (Allow extra for evaporation).

E Activation of the Column

1 Pipet 25.0 ml of the column-activation nitrate solution (1.0 ml = 0.001/mg nitrate nitrogen) into a 250 ml Erlenmeyer flask.

2 Add 75 ml concentrated ammonium chloride - EDTA solution and mix.

3 Place a 250 ml beaker under the

column and, if necessary, bring the level of storage solution in the column down to the top of the granules.

4 Place a graduated cylinder under the column.

5 Fill the cup of the column, using the mixture prepared in 1 and 2 (above).

6 Unscrew the stop-flow clamp and time the flow rate. If the rate is not between 7-10 ml per minute, adjust the screw clamp which regulates flow until the rate is achieved.

7 Continue the flow through the column until all the mixture prepared in 1 and 2 (above) has been added, and the level of solution is about 0.5 cm above the top of the granules. Stop the flow. Any collected mixture should be discarded.

8 Measure and pour into the column about 40 ml dilute ammonium chloride - EDTA solution. Repeat step 6 and 7 (above) procedures. This "washes" the column-activation nitrate solution off the granules. If you had to do much adjusting to get the correct flow rate in the step 6 procedure, do a second rinse with about 40 ml fresh, dilute ammonium chloride - EDTA solution and using the step 6 and 7 (above) procedures.

9 The column is now ready for use.

V REMOVAL OF INTERFERENCES FROM SAMPLES - AS NECESSARY

A Turbidity

1 Filter about 200 ml sample through a glass fiber filter or a 0.45 μm membrane filter. Alternatively, use the following steps 2 through 5.

2 Add 2 ml zinc sulfate solution to 200 ml sample and thoroughly mix.

3 Add 0.8-1 ml (16-20 drops) 6N sodium hydroxide solution to bring the pH to 10.5 (Use a pH meter).

4 Allow the heavy, flocculent precipitate to settle by letting the treated sample stand a few minutes.

5 Filter the supernatant through a glass fiber filter or a 0.45 μm membrane filter.

B Oil and Grease

1 Adjust the pH of about 200 ml of a non-turbid sample to 2 by addition of conc. hydrochloric acid. (Use a pH meter).

2 Place the sample in a 500 ml separatory funnel.

3 Add 50 ml of a non-polar solvent, such as freon or chloroform.

4 Shake gently to extract the oil and grease.

5 Allow the solvent layer to separate.

6 Collect the solvent layer in a 100 ml beaker and discard it.

7 Repeat steps 3-6 with a fresh, 50 ml portion of solvent.

8 The sample remaining in the separatory funnel is now ready for testing.

VI DETERMINATION OF NITRATE PLUS NITRITE

A Preparation of Nitrate Calibration Standards

1 Mark six 100 ml volumetric flasks with the concentrations listed in Table 1, column 2.

2 Using volumetric pipets, measure the amounts of standard nitrate solution listed in Table 1 into the corresponding 100 ml volumetric flask.

TABLE 1

Use these mls St'd NO_3^- Sol/100 ml	For this conc., mg NO_3^--N/1	Absorbances
0.0 ml	0.00	
0.5 ml	0.05	
1.0 ml	0.10	
2.0 ml	0.20	
5.0 ml	0.50	
10.0 ml	1.00	
SAMPLE		

3 Add enough distilled water to bring each solution to the 100.0 ml mark. Stopper and mix thoroughly.

4 Note: One flask contains 100 ml distilled water (0.00 mg NO_3-N/1). It is the reagent blank.

5 Mark six 150 ml beakers with the concentrations listed in Table 1, column 2.

6 Transfer each calibration standard to the corresponding beaker.

B pH Adjustment of Standards and Sample

1 Transfer about 200 ml sample to a 400 ml beaker.

a Any treatment required to remove interferences should have been completed prior to this step.

b Samples may require dilution if the nitrate nitrogen concentration exceeds 1 mg/liter.

1) Use a 100 ml volumetric flask and a pipet for each dilution.

2) Record the ml sample used in the dilution to 100 ml.

3) Transfer the diluted sample to a 150 ml beaker.

4) Save the remainder of sample in the 400 ml beaker. It will be required for the nitrite determination.

2 Use a meter to check the pH of each solution. If necessary, adjust the pH to between 5 and 9 with either conc. hydrochloric acid or conc. ammonium hydroxide.

C Reduction of Nitrate to Nitrite in Standards and Sample plus Color Development

1 Process the 0.00 mg/liter nitrite-nitrogen standard (reagent blank). each standard and sample using the following steps.

2 Pipet 25.0 ml of the reagent blank, standard or sample into a 250 ml Erlenmeyer flask labeled with the concentration of the standard or the code of the sample.

3 Add 75 ml concentrated ammonium chloride-EDTA solution to the same flask and mix well by swirling.

4 Place a graduated cylinder (at least 25 ml capacity) under the column.

5 Fill the cup of the column, using the mixture prepared in 2 and 3 (above).

6 Open the stop-flow clamp.

7 Again, check that the flow rate is 7-10 ml/minute and make any adjustments necessary to achieve this flow.

8 Use the stop flow clamp when 25 ml has been collected. Discard this "wash".

9 Pour the rest of the mixture prepared in 2 and 3 (above) into the column cup.

10 Rinse the Erlenmeyer flask. Discard the rinse and shake out excess distilled water.

11 Place the flask under the column and collect the rest of the mixture. Stop the flow when the solution is about 0.5 cm above the top of the granules. The flask contains nitrite in solution, i.e., any nitrite in the original sample, plus the nitrite formed by the column's reduction of nitrate in the original samples.

12 IMMEDIATELY, pipet 50.0 ml of the reduced standard or sample into a clean, labeled, 100 + ml flask or beaker. (NOTE: Nitrite can oxidize back to nitrate).

13 Add 2.0 ml color reagent and mix thoroughly by swirling.

14 The mixture should stand at least 10 minutes, and not more than two hours before spectrophotometric measurements. This allows time to repeat steps 2 through 13 for each standard and sample so all spectrophotometric measurements can be done at the same time. (More than one column can be used by analysts experienced in performing the test).

15 Repeat steps 2 through 14 for each standard and sample.

D Spectrophotometric Measurements

1 Absorbance measurements must be made within two hours of the addition of the color reagent.

  a The instrument must be warmed up.

  b Use the 540 nm wavelength.

  c Use the 0.00 mg/liter nitrate-nitrogen standard (reagent blank) to calibrate the instrument.

2 Record the absorbances in Table 1 (A.2. above) next to the corresponding concentrations of the standards. A space is also provided for recording the absorbance of the sample.

E Calibration Curve

1 Obtain a piece of graph paper and label the axes. The longer side should be labeled with the concentrations of the standards as given in Table 1. The shorter axis is labeled from 0.00 to 1.00 as the absorbance axis.

2 Use the absorbances recorded for the standards in Table 1 and the corresponding concentration of the standards to plot a calibration curve.

3 Title the graph, "Total Nitrate Plus Nitrite."

F Results

1 Use the absorbance value recorded in Table 1 for the sample to find the concentration of total nitrate plus nitrite nitrogen from the curve.

2 If a dilution was used, calculate the dilution factor and apply it to the concentration you found for the sample by using the curve.

  a Dilution Factor =

$$\frac{100 \text{ ml}}{\text{ml sample used in dilution}}$$

  b Example: You diluted 25 ml sample to 100 ml. The concentration found by using the curve was 0.4 mg/liter. Then:

Total $NO_3 + NO_2$-N mg/l =

$$\frac{100}{25} \times 0.4 \text{ or } 1.6$$

3 If more than one dilution was tested, use the result that falls nearest the middle of the curve.

VII Determination of Nitrite

A Preparation of Nitrite Calibration Standards

1 Mark six 100 ml volumetric flasks with the concentrations listed in Table 2, column 2.

2 Using volumetric pipets, measure the amounts of standard nitrite solution listed in Table 2 into the corresponding 100 ml volumetric flask.

TABLE 2		
Use these mls St'd NO_2^- sol/100 ml	For this conc., mg NO_2-N/l	Absorbance
0.0 ml	0.00	
0.5 ml	0.05	
1.0 ml	0.10	
2.0 ml	0.20	
5.0 ml	0.50	
10.0 ml	1.00	
SAMPLE		

3 Add enough distilled water to bring each solution to the 100.0 ml mark. Stopper and mix thoroughly.

4 Note: One flask contains 100 ml distilled water (0.00 mg NO_2-N). It is the reagent blank.

5 Mark six 150 ml beakers with the concentrations listed in Table 2, column 2.

6 Transfer each calibration standard to the corresponding beaker.

B pH Adjustment of Standards and Sample

1 You should have reserved 100-175 ml of undiluted sample from VIB (above).

a Nitrite concentrations are usually well within the applicability of this test so sample dilution is usually not required.

2 Use a meter to check the pH of the sample and of each nitrite standard solution. If necessary, adjust the pH to between 5 and 9 with either conc. hydrochloric acid or conc. ammonium hydroxide.

C Color Development

1 Label clean, 250 ml flasks with the concentrations of the standards or the sample code.

2 Pipet 25.0 ml of the reagent blank, each standard and sample into its corresponding flask.

3 Add 75 ml concentrated ammonium chloride - EDTA solution to each and mix well by swirling.

4 Pipet 50.0 ml of each standard and sample mixture prepared in 2 and 3 into a clean, labeled 100+ ml flask.

5 Add 2.0 ml color reagent to each and mix thoroughly by swirling.

6 Each mixture should stand at least 10 minutes (but not more than two hours) before spectrophotometric measurements.

D Spectrophotometric Measurements

1 The instrument must be warmed up.

2 Use the 540 nm wavelength.

3 Use the 0.00 mg/liter nitrite nitrogen standard (reagent blank) to calibrate the instrument.

4 Record the absorbances in Table 2 (A2. above) next to the corresponding concentrations of the standards. A space is also provided for recording the absorbance of the sample.

E Calibration Curve

1 Obtain a piece of graph paper and label the axes. The longer side should be labeled with the concentrations of the standards as given in Table 2. The shorter axis is labeled from 0.00 to 1.00 as the absorbance axis.

2 Use the absorbances recorded for the standards in Table 2, and the corresponding concentration of the standards to plot a calibration curve.

3 Title the graph "Nitrite"

F Results

1 Use the absorbance value recorded in Table 2 for the sample to find the concentration of nitrite nitrogen from the curve.

2 A dilution was probably not necessary. If it was required, calculate the dilution factor and apply it to the concentration you found for the sample by using the curve.

a Dilution Factor =

$$\frac{\text{final dilution volume}}{\text{ml sample used in dilution}}$$

VIII CHECKING COLUMN EFFICIENCY

A In order to validate results, check the efficiency of the reduction column by comparing at least one reduced nitrate standard to a nitrite standard of the same concentration.

1 % efficiency =

$$\frac{\text{absorbance of } NO_3\text{St'd*}}{\text{absorbance of } NO_2\text{St'd*}} \times 100$$

* Standards of equal concentration

2 The value is acceptable if it is between 96 and 104%.

3 The best representation of column efficiency is the average of the % efficiencies, calculated by comparing every pair(5) of NO_3 and NO_2 standards of equal concentration.

B If the column efficiency is acceptable, report the results as required. See Section IX.

C If the % efficiency of the reduction column is not within the acceptable range, you should remove the copperized cadmium from the column, add a few grams of cadmium (new or used) and repeat all of section IV, "Preparation of Reduction Column" (above).

IX REPORTING RESULTS

The results from this test can be used in a variety of ways to report nitrate-nitrite concentrations.

A Total Nitrate plus Nitrite Nitrogen

1 Report the results from section VI F

B Nitrite Nitrogen

1 Report the results from section VII F

C Nitrate Nitrogen

1 Subtract the result for nitrite nitrogen (VII F) from the result for total nitrate plus nitrate nitrogen (VI F) for each sample.

D Nitrate

1 Calculate the concentration of nitrate nitrogen in the sample as described in C. (above).

2 Multiply this concentration by 4.43

E Nitrite

1 Multiply the result for each sample from section VII F by 3.29

REFERENCE

1 Methods for Chemical Analysis of Water and Wastes, 1974, USEPA - EMSL, Cincinnati, Ohio 45268

This outline was prepared by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, USEPA, Cincinnati, Ohio 45268

Descriptors: Analytical Techniques, Chemical Analysis, Laboratory Tests, Nutrients, Nitrate, Nitrite, Nitrogen, Water Analysis

LABORATORY PROCEDURE FOR TOTAL SOLIDS

I INTRODUCTION

A This procedure was excerpted from Methods for Chemical Analysis of Water and Wastes, 1979, Environmental Protection Agency, Office of Water Programs, Analytical Quality Control Laboratory.

B The procedure is applicable to surface and saline waters, domestic and industrial wastes.

C The practical range of the determination is 10-20,000 mg/L.

D Nonhomogenous materials (large floating particles or submerged agglomerates) should be excluded from the sample. Floating grease and oil should be included in the sample and dispersed in a blender before measuring the aliquot.

E Samples should be analyzed as soon as possible.

II EQUIPMENT

A Porcelain, Vycor, or platinum evaporating dishes, 100 - 150 ml capacity; smaller sizes may be used as required.

B Muffle furnace, $550 \pm 50^{\circ}C$

C Drying oven, $103 - 105^{\circ}C$

D Desiccator

E Analytical balance

F Steam bath or Oven at 98°C

G Graduated cylinder, 100 ml

III PROCEDURE

CAUTION· Fingerprints on the dish can result in weighing errors. Use tongs or a tissue to handle the dish throughout the procedure.

A Heat the clean evaporating dish in a muffle furnace at 550 ± 50°C for 1 hour.

B Cool the dish in a desiccator.

C Store the dish in the desiccator and weigh just before use.

D Weigh the dish on an analytical balance. (Use tongs or tissue to handle the dish).

E Shake the sample container vigorously.

F Measure 100 ml of the well-mixed sample in a graduated cylinder. (At least 25 mg of residue should be obtained; less volume of sample may be used if the sample appears to be high in solids content. If it is low in solids content, more sample may be added to the dish after drying the first aliquot).

G Rapidly, but without spilling, pour the sample into the evaporating dish.

H Rinse the cylinder with 10-15 ml distilled water, adding the rinse to the dish.

I Dry the sample on a steam bath, or at 98°C (to prevent boiling and splattering) in the oven.

J Dry the evaporated sample in the oven at 103 - 105°C for at least one hour.

K Cool the dish in the desiccator and then weigh it. (Use tongs or tissue to handle the dish).

L Repeat the heating at 103 - 105°C, cooling and weighing until the weight loss is less than 4% of the previous weight or 0.5 mg, whichever is less.

OUTLINE IS CONTINUED ON
NEXT PAGE

IV CALCULATIONS

$$\text{mg total solids/L} = \frac{(\text{wt dish} + \text{residue})^{*} - (\text{wt dish})^{*} \times 1000 \times 1000}{\text{ml of sample}}$$

* in grams

This outline was prepared by C. R. Feldmann, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Analytical Techniques, Chemical Analysis, Laboratory Tests, Solids, Water Analysis

LABORATORY PROCEDURE FOR SUSPENDED (NON-FILTERABLE) SOLIDS

I INTRODUCTION

A This procedure was excerpted from Methods for Chemical Analysis of Water and Wastes, 1979, Environmental Protection Agency, Methods Development and Quality Assurance Laboratory.

B The procedure is applicable to surface and saline waters, domestic and industrial wastes.

C The practical range of the determination is 10 - 20000 mg/L.

D All nonhomogenous particulates (such as leaves, sticks, fish and lumps of fecal matter) should be excluded from the sample.

E Sample preservation is not practical; the analysis should be done as soon as possible.

II EQUIPMENT

A Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder. Gelman A/E, Millipore AP-40, Reeves Angel 934-AH, or equivalent.

B Membrane filter funnel (for use with the 4.7 cm disc), or a 25 ml Gooch crucible (for use with the 2.2 cm disc) and crucible adapter.

C Planchet to support filter disc during drying

D Graduated cylinders, 25 ml and 100 ml

E 500 ml suction flask with hose and pinch clamp

F Drying oven, 103 - 105°C

G Desiccator

H Analytical balance, 200 g capacity, capability of weighing to 0.1 mg

III PROCEDURE

CAUTION: Fingerprints on the Gooch crucible can result in weighing errors. Use tongs or a tissue to handle it.

A Assemble the filtering apparatus and suction flask (either the 2.2 cm disc, Gooch crucible and adapter;* or the 4.7 cm disc and membrane filter funnel).

B Apply suction to the flask and wash the disc with three successive 20 ml portions of distilled water.

C Continue the suction until all water has passed through the disc.

D Remove the Gooch crucible plus 2.2 cm disc, wipe the outside thoroughly, and dry in the oven at 103 - 105°C for one hour, or,

E Remove the 4.7 cm disc from the membrane filter funnel onto a planchet and dry in the oven at 103 - 105°C for one hour. In D or E if the disc is not to be used immediately, store it in the desiccator.

F Close to the time of use, weigh the 4.7 cm disc or 2.2 cm disc plus Gooch crucible. (Use tongs or tissue to handle the crucible). Repeat the drying cycle until a constant weight is obtained. See "Note" on next page.)

G Assemble the filtering apparatus.

H Apply suction to the flask.

I Wet the filter disc.

J Shake the sample container vigorously.

K Measure 100 ml of the well mixed sample in a 100 ml graduated cylinder. (If the sample appears to be low in solids, a larger volume may be used).

L Rapidly, but without spilling, pour the sample into the funnel or crucible.

M Continue the suction until all of the water has passed through the disc.

N Use about 10 ml of distilled water to rinse the graduated cylinder into the filter funnel.

O Rinse the filter funnel walls with distilled water.

P Rinse the solids with distilled water.

Q Remove all traces of water by continuing to apply vacuum.

R Remove the 4.7 cm disc from the funnel, place it on a planchet (or watch glass), and dry in the oven at 103 - 105°C to to constant weight, or

S Remove the Gooch crucible plus 2.2 cm disc and dry in the oven at 103 - 105°C to constant weight. (Use tongs or a tissue to handle the crucible).

Note: Drying to constant weight refers to the process of:

1) Drying the disc (or disc plus crucible) at 103 - 105°C
2) cooling in the desiccator
3) weighing
4) repeating steps 1), 2), and 3).

If there is no difference in the two final weights, the disc (or disc plus crucible) has been dried to constant weight. Weights that agree within 0.5 mg are acceptable. In practice the initial drying period is sometimes extended to several hours to ensure complete drying.

IV CALCULATIONS

mg nonfilterable (suspended) solids/L

$$\frac{(\text{wt of 4.7 cm disc + residue})^* - (\text{wt of 4.7 cm disc})^* \times 1000 \times 1000}{\text{ml of sample filtered}}$$

or

$$\frac{(\text{wt of 2.2 cm disc + Gooch crucible + residue})^* - (\text{wt of 2.2 cm disc + Gooch crucible})^* \times 1000 \times 1000}{\text{ml of sample filtered}}$$

*in grams

REFERENCE

1. Methods for Chemical Analysis of Water and Wastes, 1979, U.S. EPA, MDQARL, Cincinnati, Ohio 45268.

This outline was prepared by C. R. Feldmann, Chemist, National Training and Operational Technology Center, and revised by Audrey D. Kroner, Chemist, National Training & Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Analytical Techniques, Chemical Analysis, Laboratory Tests, Solids, Water Analysis

Laboratory Data Sheet
for
TOTAL SUSPENDED (NON-FILTERABLE) SOLIDS, mg/liter

Name of Plant ______________________

STEP	SUSPENDED SOLIDS	SAMPLE	SAMPLE	EXAMPLE	
	Identification			INS #1	1
	Type (grab, etc.)			GRAB	2
	Date & Time Collected			5/1/74 0900	3
	Sample Collector			Tom Sampler	4
	Filter Identification			WG2	5
	Date & Time Analysis began			5/1/74 1100	6
	ml Sample Filtered			67.0	7
	1st weight of Filter* plus Residue (g)			0.1426	8
	2nd weight of Filter* plus Residue (g)			0.1416	9
	Difference (1st-2nd)			0.0010	10
	3rd weight of Filter* plus Residue (g)			0.1413	11
	Difference (2nd-3rd)			0.0003	12
	Final weight of Filter* plus Residue (g)			0.1413	13
	Weight of Filter* (g)			0.1293	14
	Find Difference (g) by subtracting Line 14 from Line 13			0.0120	15
	Divide to 7 decimal places: $\frac{\text{(line 15) difference (g)}}{\text{(line 7) ml sample filtered}}$			0.0001791	16
	Multiply Line 16 by 1000 000 (move decimal point 6 places Rt.)			179.1	17
	Round answer on Line 17 to nearest whole number			179 mg/l	18
	Analyst			Mary Analyst	19

*"Filter" means the filter disc if a funnel type filtration assembly is used. If Gooch crucibles are used "filter" means the crucible containing a filter disc.

CALIBRATION AND USE OF A TURBIDIMETER (NEPHELOMETER)

I REAGENTS(1)

A Turbidity - free water - Pass distilled water through a 0.45 μm pore size membrane filter if such filtered water shows a lower turbidity than the original distilled water.

B Stock Turbidity Suspension - 400 units

1 Directions are for preparing 100.0 ml. Larger volumes may be required.

2 Solution, 1: Dissolve 1.00g hydrazine sulfate, $(NH_2)_2 \cdot H_2SO_4$, in turbidity free water and dilute to 100ml in a volumetric flask.

3 Solution 2: Dissolve 10.00g hexamethylenetetramine in turbidity-free water and dilute to 100ml in a volumetric flask.

4 Suspension: Mix 5.0ml Solution 1 with 5.0ml Solution 2 in a 100 ml volumetric flask. Allow to stand for 24 hours at 25 ± 3°C. Dilute to the mark and mix.

5 Stability: Prepare a new stock suspension each month.

C Standard Turbidity Suspension - 40 units

1 Dilute 10.00ml stock turbidity suspension to 100ml with turbidity - free water in a 100 ml volumetric flask. The turbidity is defined as 40 units.

2 Stability: Prepare a new standard suspension each week.

D Dilute Standard Turbidity Suspension - 4 units

1 Dilute 1.0 ml stock turbidity suspension to 100 ml with turbidity-free water in a 100 ml volumetric flask. The turbidity should be 4 units.

2 Stability: Prepare a new standard suspension each week.

E Secondary Standards

1 Solutions standardized with Formazin can be purchased from the manufacturer of the instrument.

2 Date such solutions. Store under the conditions specified. Discard and replace when flocculation in the solution is observed or when it fails a periodic check with a Formazin Standard. (2)(3)

II PREPARATIONS FOR MEASUREMENTS

A Suspensions

1 Check date of preparation and prepare fresh solutions if required.

B Sample Cell (5)

1 Cells should be cleaned immediately after use as described in V.B. below.

2 Inspect cells for cleanliness. If necessary, clean them using V.B. below.

3 Check cells for scratches and etching. Discard those with imperfections.

C Instrument

1 Scale - If a scale is inserted, check that it is in the correct position. If the scale is blank, construct a calibration scale for each range on the instrument. (See III B).

2 Zero - Adjust meter needle to zero point on scale as directed by manufactuer.

3 Lens - Check for cleanness. If required, follow manufacturer's instructions for removing and cleaning the lens. Accurate re-positioning of the lens is critical for accurate measurements.

4 Warm-Up Period - Follow manufacturer's instructions. Continuous running is often suggested because of the photomultiplier tubes.

5 Focus - Use template or method described by manufacturer to check and, if necessary, set the focus.

D Determine Range of Sample Turbidity

1 Use steps 5 through 16 in III A below EXCEPT Step 12 which should be: Obtain a turbidity reading from the scale.

2 Note which Range (instrument scale) best "brackets" the turbidity of each sample.

3 If the turbidity of a sample exceeds 40 units, use the higher scales provided to determine the dilution required so the final reading will be below 40 units. For final measurements, use the Range (Scale) appropriate for the diluted sample.

III INSTRUMENT CALIBRATION AND MEASUREMENTS(1)

A Pre-Calibrated Scale

1 Each week, prepare at least one standard for the required instrument range (s) (as determined in II. D. above) by diluting one of the Formazin suspensions described above in I, Reagents. The table below gives "EXAMPLE DILUTIONS".

2 Set the instrument RANGE knob at the first range to be tested. (The instrument should be ON, warmed up, zeroed, etc., as in II C above).

3 Make any instrument adjustment specified by the manufacturer to use this RANGE.

4 Rinse the SAMPLE CELL 2 times with the appropriate suspension (or sample).

5 Shake the suspension to thoroughly disperse the solids. (For secondary standards, check the manufacturer's instructions for this step).

EXAMPLE DILUTIONS

NO.	EXAMPLE INSTRUMENT RANGES	VOLUME	TURBIDITY STANDARD	FINAL DILUTION	FINAL TURBIDITY
1	0 - 0.1	2.5 ml	4 unit	100.0 ml	0.1
2	0 - 0.2	5.0 ml	4 unit	100.0 ml	0.2
3	0 - 0.3	7.5 ml	4 unit	100.0 ml	0.3
4	0 - 1	2.5 ml	40 unit	100.0 ml	1
5	0 - 3	7.5 ml	40 unit	100.0 ml	3
6	0 - 10	25.0 ml	40 unit	100.0 ml	10
7	0 - 30	7.5 ml	400 unit	100.0 ml	30
8	0 - 100	25 ml	400 unit	100.0 ml	100
9	0 - 300	75 ml	400 unit	100.0 ml	300
10	0 - 400	100 ml	400 unit	100.0 ml	400
11	0 - 1000	100 ml	400 unit	100.0 ml	400

6 Wait until air bubbles disappear in the suspension.

7 Pour the suspension into the SAMPLE CELL up to the level specified by the manufacturer. CAUTION: Always hold the cell above the area from which light scattering is measured.

8 If applicable, screw cap on cell.

9 Wipe the outside of the cell with a lint-free tissue.

10 Examine the suspension in the cell to check for air bubbles. If air bubbles are present, eliminate them:

- a by inserting the cell (5) in the sample holder and waiting a few minutes so bubbles rise above photomultiplier tube. CAUTION: More bubbles can form if a temperature rise occurs.
- b by holding the cell at the top and:
  - 1 flicking side with your finger or
  - 2 dipping the end of the cell into an ultrasonic cleaning bath or
  - 3 centrifuging the filled cell in cups with rubber cushions and surrounded with water.
  - 4 NOTE: After any of these remedies, again wipe the outside of the cell. When air bubbles are gone, insert the (5) cell in the sample holder.

11 Place the LIGHT SHIELD according to the manufacturer's instruction.

12 Use the STANDARDIZING control to obtain a meter reading corresponding to the turbidity of the standard suspension.

13 Remove the LIGHT SHIELD.

14 Remove the SAMPLE CELL.

15 Discard the standard suspension.

16 Rinse SAMPLE CELL 2 times with turbidity - free water.

17 Use Steps 4 through 11 for each sample (or diluted sample) to be tested in this range. For samples, step 12 should be : Record the turbidity reading for the sample. Then do Steps 13 through 16 as above.

NOTE: The final reading for samples should not exceed 40 NTU. If this reading is exceeded for a sample, dilute it and repeat the calibration/measurement procedure above using the appropriate range and standard. (Selection of the range as described in II. D. above should make this unnecessary at this stage of the procedure).

B Non-Calibrated Scale

Prepare a series of standards and make a calibration scale for each range of the instrument.

- a The instrument should be ON, warmed up, zeroed, etc., as in II C above.
- b Prepare enough standards to give several points on each scale so estimated readings can be reasonably accurate.
- c Use the table of EXAMPLE DILUTIONS in III A above to prepare the highest standard for each instrument range. The rest of each calibrating series can also be prepared by dilutions based on the information in the table.

2 Self-prepared scales should also be calibrated each day using the procedure given in III A above for pre-calibrated scales.

3 Self-prepared scales are used for samples in the manner described in III A above for pre-calibrated scales.

IV CALCULATION/RESULTS(1)

A Diluted Samples

Multiply final sample readings by the appropriate dilution factor.

B Reporting Results

Report results as follows:

NTU	Report to Nearest:
0.0 - 1.0	0.05
1 - 10	0.1
10 - 40	1
40 - 100	5
100 - 400	10
400 - 1000	50
> 1000	100

C Precision and Accuracy

1 In a single laboratory (MDQARL), using surface water samples at levels of 26, 41, 75 and 180 NTU, the standard deviations were ± 0.60, ± 0.94, ± 1.2 and ± 4.7 units, respectively.

2 Accuracy data is not available at this time.

V STORAGE

A Standard Suspensions

1 Store in glass containers at room temperature.

2 Excess light or heat may affect stability.

3 Observe stability times noted for each in I. above.

B Sample Cells

1 Discard cells with scratches or etching.

2 Clean cells immediately after use with this order of treatments:(4)

- a detergent
- b organic solvents, if required
- c deionized water
- d alcohol or acetone rinses to dry
- e lint-free tissue, if required

3 Store in a manner to protect the cells from scratches.

C Instrument

1 A line operated instrument should be permanently located so moving it often is not necessary.

2 Turbidimeters should be protected from dust, especially the lens system.

3 Store any removable parts as directed by manufacturer.

4 Close any access doors.

5 Because of the photomultiplier tubes, the manufacturer may suggest continuous running of the instrument to insure maximum accuracy for measurements. Frequency of use can determine the actual routine for warm-up time.

6 Follow any other storage directions in the manufacturer's manual.

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, EPA-EMSL Cincinnati, Ohio 45268, 1979.

2 Laboratory Turbidimeter, Model 2100A, Hach Chemical Co., Ames, Iowa, 1973.

3 Turbidimeters, Information Circular No. 373A, Fisher Scientific Company, Pittsburgh, PA

4 Handbook for Analytical Quality Control, EPA-EMSL, Cincinnati, Ohio 45268, 1979.

5 The orientation of the sample cell should be identical each time it is placed in the instrument. Mark the cell and instrument to ensure that the cell is oriented consistently. Use the same cell throughout the procedure.

This outline was prepared by Audrey D. Kroner, Chemist, National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Analytical Techniques, Laboratory Tests, Turbidity

CALIBRATION AND USE OF A CONDUCTIVITY METER

I EQUIPMENT AND REAGENTS

A Equipment

1 Solu Bridge conductivity meters

2 Probes

- a Cell VSO2
- b Cell VS2
- c Cell VS2O

3 Thermometers

4 400 ml beakers

B Reagents

1 Standard KC1 solutions

Normality of KC1 Solution	Specific Conductance micromhos/cm.
0.0001	14.9
0.001	147.0
0.01	1413.0
0.1	12900.0

2 Distilled water

II CHECKING THE INSTRUMENT

A The measurement of specific conductivity as presented in sections II and III is written for one type of conductivity meter and probe.

B A battery check is made by depressing the Battery Check switch, and at the same time pressing the on-off button. The meter needle should deflect to the right (positive) and come to rest in the green zone.

C Place a 10,000 ohm resistor in the holes of the electrical contacts on the meter. Turn the temperature knob to read 25°C. Depress the on-off button and bring the meter needle to a reading of 0 by turning the specific conductance switch. The specific conductance reading should be approximately 200 micromhos/cm.

III DETERMINATION OF THE CALIBRATION CONSTANT

A Determine the temperature of the standard KC1 solutions and move the temperature knob to that value.

B Connect probe Cell VS02 to the conductivity meter.

C Rinse the probe in the beaker of distilled water, wipe the excess water with a kimwipe and place probe in the first beaker of KC1 solution (0.0001 N).

D Make certain the cell is submerged to a point at least 1/2 inch above the air hole and that no entrapped air remains. The cell should also be at least 1/2 inch from the inside walls of the flask.

E Press and hold down the ON-OFF button, simultaneously rotating the main scale knob until the meter reads zero. Release the button. (If the meter needle remains off scale or cannot be nulled, discontinue testing in that solution.)

F Record the scale reading in Table 1 and proceed to KC1 solutions 0.001N, 0.01N, 0.1 N using Steps C, D and E.

G Repeat steps C through F using the VS2, then the VS20 probe.

H Compute the cell calibration constant-a factor by which scale readings must be multiplied to compute specific conductance:

$K_{sp} = cM$

where K_{sp} = actual specific conductance,

c = calibration constant

M= meter reading

(continued next page)

Cell Number	Relative Conductivity Value	Maximum range micromhos/cm	Most accurate range micromhos/cm
Cell VSO2	1	0 - 50	2 - 30
Cell VS2	10	0 - 500	20 - 300
Cell VS2O	100	0 - 5000	200 - 3000

TABLE I DATA FOR CALIBRATION CONSTANTS

Probe	Cell VSO2				Cell VS2				Cell VS2O			
KCl Solutions	0.0001N	0.001N	0.01N	0.1N	0.0001N	0.001N	0.01N	0.1N	0.0001N	0.001N	0.01N	0.1N
Test # 1												
Cell Constant												

For each cell, calculate the cell constant by using the meter reading closest to the 400 - 600 range. The known specific conductance for the corresponding KCl solution can be found in IB Reagents. Record the cell constants on Table I.

IV DETERMINATION OF K_{sp} FOR SAMPLES

Obtain meter readings, M, for samples A, B and C using Section III C, D and E. Record M in Table 2. See Table I for the appropriate cell constant, c, to calculate K_{sp} for each sample where $K_{sp} = cM$. Record results in Table 2.

V EPA METHODOLOGY

The current EPA Manual(1) specifies using the procedures found in Refenences 2 and 3. These procedures have been adapted for this laboratory session and all are approved in 40CFR136 for NPDES report purposes.

ACKNOWLEDGMENT

This outline contains certain portions of previous outlines by Messrs. J. W. Mandia, and J. R. Tilstra.

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, USEPA, AQCL, Cincinnati, OH 45268, 1974.

2 Standard Methods for the Examination of Water and Wastewater, 14th Edition. 1976.

3 Book of ASTM Standards, Part 31, 1975.

This outline was prepared by C. R. Feldmann, Chemist, National Training and Operational Technology Center, and revised by Audrey D. Kroner, also with National Training and Operational Technology Center, OWPO, USEPA, Cincinnati, Ohio 45268.

Descriptors: Analytical Techniques, Conductivity, Electrical Conductance, Specific Conductivity, Water Analysis.

TABLE 2. SPECIFIC CONDUCTIVITY TESTS

Sample	A			B			C		
Probe	Cell VSO2	Cell VS2	Cell VS2O	Cell VSO2	Cell VS2	Cell VS2O	Cell VSO2	Cell VS2	Cell VS2O
1									
Cell Constant									
Sp. Cond. µmhos/cm									

LABORATORY SAFETY PRACTICES

I INTRODUCTION

A Safe Use, Handling and Storage of Chemicals

1 Chemicals in any form can be safely stored, handled, and used if their hazardous physical and chemical properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment are observed.

2 The management of every unit within a manufacturing establishment must give wholehearted support to a well integrated safety policy.

B General Rules for Laboratory Safety

1 Supervisory personnel should think "safety." Their attitude toward fire and safety standard practices is reflected in the behavior of their entire staff.

2 A safety program is only as strong as the worker's will to do the correct things at the right time.

3 The fundamental weakness of most safety programs lies in too much lip service to safety rules and not enough action in putting them into practice.

4 Safety practices should be practical and enforceable.

5 Accident prevention is based on certain common standards of education, training of personnel and provision of safeguards against accidents.

II LABORATORY DESIGN AND EQUIPMENT

A Type of Construction

1 Fire-resistant or noncombustible

2 Multiple story buildings should have adequate means of exit.

3 Stairways enclosed with brick or concrete walls

4 Laboratories should have adequate exit doors to permit quick, safe escape in an emergency and to protect the occupants from fires or accidents in adjoining rooms. Each room should be checked to make sure there is no chance of a person being trapped by fire, explosions, or release of dangerous gases.

5 Laboratory rooms in which most of the work is carried out with flammable liquids or gases should be provided with explosion-venting windows.

B Arrangement of Furniture and Equipment

1 Furniture should be arranged for maximum utilization of available space and should provide working conditions that are efficient and safe.

2 Aisles between benches should be at least 4 feet wide to provide adequate room for passage of personnel and equipment.

3 Desks should be isolated from benches or adequately protected.

4 Every laboratory should have an eye-wash station and a safety shower.

C Hoods and Ventilation

1 Adequate hood facilities should be installed where work with highly toxic or highly flammable materials are used.

2 Hoods should be ventilated separately and the exhaust should be terminated at a safe distance from the building.

3 Make-up air should be supplied to rooms or to hoods to replace the quantity of air exhausted through the hoods.

4 Hood ventilation systems are best designed to have an air flow of not less than 60 linear feet per minute across the face of the hood, with all doors open and 150, if toxic materials are involved.

5 Exhaust fans should be spark-proof if exhausting flammable vapors and corrosive resistant if handling corrosive fumes.

6 Controls for all services should be located at the front of the hood and should be operable when the hood door is closed.

7 All laboratory rooms should have the air changed continuously at a rate depending on the materials being handled.

D Electrical Services

1 Electrical outlets should be placed outside of hoods to afford easy access and thus protect them from spills and corrosion by gases.

2 Noninterchangeable plugs should be provided for multiple electrical services.

3 Adequate outlets should be provided and should be of the three-pole type to provide for adequate grounding.

E Storage

1 Laboratories should provide for adequate storage space for mechanical equipment and glassware which will be used regularly.

2 Flammable solvents should not be stored in glass bottles over one liter in size. Large quantities should be stored in metal safety cans. Quantities requiring containers larger than one gallon should be stored outside the laboratory.

3 Explosion proof refrigerators should be used for the storage of highly volatile and flammable solvents.

4 Cylinders of compressed or liquified gases should not be stored in the laboratory.

F Housekeeping

1 Housekeeping plays an important role in reducing the frequency of laboratory accidents. Rooms should be kept in a neat orderly condition. Floors, shelves, and tables should be kept free from dirt and from all apparatus and chemicals not in use.

2 A cluttered laboratory is a dangerous place to work. Maintenance of a clean and orderly work space is indicative of interest, personal pride, and safety-mindedness.

3 Passageways should be kept clear to all building exits and stairways.

4 Metal containers should be provided for the disposal of broken glassware and should be properly labeled.

5 Separate approved waste disposal cans, should be provided for the disposal of waste chemicals.

6 Flammable liquids not miscible with water and corrosive materials, or compounds which are likely to give off toxic vapors should never be poured into the sink.

G Fire Protection

1 Laboratory personnel should be adequately trained regarding pertinent fire hazards associated with their work.

2 Personnel should know rules of fire prevention and methods of combating fires.

3 Fire extinguishers (CO_2 type) should be provided at convenient locations and personnel should be instructed in their use.

4 Automatic sprinkler systems are effective for the control of fires in chemical laboratories.

H Alarms

1 An approved fire alarm system should be provided.

2 Wherever a hazard of accidental release of toxic gases exists, a gas alarm system to warn occupants to evacuate the building should be provided.

3 Gas masks of oxygen or compressed air type should be located near exits and selected personnel trained to use them.

III HANDLING GLASSWARE

A Receiving, Inspection and Storage

1 Packages containing glassware should be opened and inspected for cracked or nicked pieces, pieces with flaws that may become cracked in use, and badly shaped pieces.

2 Glassware should be stored on well-lighted stockroom shelves designed and having a coping of sufficient height around the edges to prevent the pieces from falling off.

B Laboratory Practice

1 Select glassware that is designed for the type of work planned.

2 To cut glass tubing or a rod, make a straight clean cut with a cutter or file at the point where the piece is to be severed. Place a towel over the piece to protect the hands and fingers, then break away from the body.

3 Large size tubing is cut by means of a heated nichrome wire looped around the piece at the point of severance.

4 When it is necessary to insert a piece of glass tubing or a rod through a perforated rubber or cork stopper, select the correct bore so that the insertion can be made without excessive strain.

5 Use electric mantels for heating distillation apparatus, etc.

6 To remove glass splinters, use a whisk broom and a dustpan. Very small pieces can be picked up with a large piece of wet cotton.

IV GASES AND FLAMMABLE SOLVENTS

A Gas Cylinders

1 Large cylinders must be securely fastened so that they cannot be dislodged or tipped in any direction.

2 Connections, gauges, regulators or fittings used with other cylinders must not be interchanged with oxygen cylinder fittings because of the possibility of fire or explosion from a reaction between oxygen and residual oil in the fitting.

3 Return empty cylinders promptly with protective caps replaced.

B Flammable Solvents

1 Store in designated areas well ventilated.

2 Flash point of a liquid is the temperature at which it gives off vapor sufficient to form an ignitible mixture with the air near the surface of the liquid or within the vessel used.

3 Ignition temperature of a substance is the minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element.

4 Explosive or flammable limits. For most flammable liquids, gases and solids there is a minimum concentration of vapor in air or oxygen below which propagation of flame does not occur on contact with a source of ignition. There is also a maximum proportion of vapor or gas in air above which

propagation of flame does not occur. These limit mixtures of vapor or gas with air, which if ignited will just propagate flame, are known as the "lower and higher explosive or flammable limits."

5 Explosive Range. The difference between the lower and higher explosive or flammable limits, expressed in terms of percentage of vapor or gas in air by volume is known as the "explosive range."

6 Vapor Density is the relative density of the vapor as compared with air.

7 Underwriter's Laboratories Classification is a standard classification for grading the relative hazard of the various flammable liquids. This classification is based on the following scale:

Ether Class	100
Gasoline Class	90 - 100
Alcohol (ethyl) Class	60 - 70
Kerosene Class	30 - 40
Paraffin Oil Class	10 - 20

8 Extinguishing agents

V CHEMICAL HAZARDS

A Acids and Alkalies

1 Some of the most hazardous chemicals are the "strong" or "mineral" acids such as hydrochloric, hydrofluoric, sulfuric and nitric.

2 Organic acids are less hazardous because of their comparatively low ionization potentials. However, such acids as phenol (carbolic acid), hydrocyanic and oxalic are extremely hazardous because of their toxic properties.

3 Classification of acids

B Oxidizing Materials

1 Such oxidizing agents as chlorates, peroxides, perchlorates and perchloric acid, in contact with organic matter can cause explosions and fire.

2 They are exothermic and decompose rapidly, liberating oxygen which reacts with organic compounds.

3 Typical hazardous oxidizing agents are:

Chlorine Dioxide
Sodium Chlorate
Potassium Chromate
Chromium Trioxide
Perchloric Acid

C Explosive Power

1 Many chemicals are explosive or form compounds that are explosive and should be treated accordingly.

2 A few of the more common examples of this class of hazardous materials are:

Acetylides
Silver Fulminate
Peroxides
Peracetic Acid
Nitroglycerine
Picric Acid
Chlorine and Ethylene
Sodium Metal
Calcium Carbide

D Toxicity

1 Laboratory chemicals improperly stored or handled can cause injury to personnel by virtue of their toxicity.

2 Types of exposure. There are four types of exposure to chemicals:

a Contact with the skin and eyes

b Inhalation

c Swallowing

d Injection

VI PRECAUTIONARY MEASURES

A Clothing and Personal Protective Equipment

1 Chemical laboratories should have special protective clothing and equipment readily available for emergency use and for secondary protection of personnel working with hazardous materials.

2 Equipment should be provided for adequate:

a Eye protection

b Body protection

c Respiratory protection

d Foot protection

e Hand protection

B Bodily Injury

1 Burns, eye injuries, and poisoning are the injuries with which laboratory people must be most concerned.

2 First emphasis in the laboratory should be on preventing accidents. This means observing all recognized safe practices using necessary personal protective equipment and exercising proper control over poisonous substances at the source of exposure.

3 So that a physician can be summoned promptly, every laboratory should have posted the names, telephone numbers, and addresses of doctors to be called in an emergency requiring medical care.

REFERENCES

Guide for Safety in the Chemical Laboratory, the General Safety Committee of the Manufacturing Chemists Association, Inc., Van Nostrand, New York (1954).

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